

SOIL SCIENCE

VOLUME 73

JANUARY TO JUNE, 1952

RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY
U. S. A.

PUBLISHED BY
THE WILLIAMS & WILKINS COMPANY
BALTIMORE, MARYLAND

SOIL SCIENCE

Founded 1916 by Jacob G. Lipman

Editor-in-Chief
FIRMAN E. BEAR

Associate Editor
HERMINIE BROEDEL KITCHEN

CONSULTING EDITORS

- WM. A. ALBRECHT
University of Missouri, Columbia, Missouri
- LYLE T. ALEXANDER
Bureau of Plant Industry, Beltsville, Maryland
- R. V. ALLISON
University of Florida, Gainesville, Florida
- F. J. ALWAY
University of Minnesota, St. Paul, Minnesota
- L. D. BAVER
Sugar Planters' Experiment Station, Honolulu
- H. H. BENNETT
Soil Conservation Service, Washington, D. C.
- G. B. BODMAN
University of California, Berkeley, California
- RICHARD BRADFIELD
Cornell University, Ithaca, New York
- R. H. BRAY
University of Illinois, Urbana, Illinois
- H. J. CONN
Agricultural Experiment Sta., Geneva, New York
- H. P. COOPER
Clemson Agr. College, Clemson, South Carolina
- O. W. DAVIDSON
Rutgers University, New Brunswick, New Jersey
- A. DEMOLON
49 Rue Geoffrey St. Hilaire, Paris, France
- E. E. DETURK
University of Illinois, Urbana, Illinois
- F. L. DULEY
University of Nebraska, Lincoln, Nebraska
- WILLARD GARDNER
Utah State Agricultural College, Logan, Utah
- V. V. GEMMERLING
Moskovskii Universitet, Moscow, U. S. S. R.
- J. E. GREAVES
Utah State Agricultural College, Logan, Utah
- H. J. HARPER
Samuel Roberts Noble Found., Ardmore, Oklahoma
- STERLING HENDRICKS
Bureau of Plant Industry, Beltsville, Maryland
- D. J. HISSINK
Bussum, Netherlands
- C. D. JEFFRIES
Pa. State College, State College, Pennsylvania
- HANS JENNY
University of California, Berkeley, California
- JACOB S. JOFFE
Rutgers University, New Brunswick, New Jersey
- W. P. KELLEY
University of California, Berkeley, California
- CHARLES E. KELLOGG
Bureau of Plant Industry, Beltsville, Maryland
- H. LUNDEGÅRDH
Lantbrukshögskolan, Uppsala, Sweden
- M. M. MCCOOL
405 Garfield St., Gary, Indiana
- W. H. MACINTIRE
University of Tennessee, Knoxville, Tennessee
- O. C. MAGISTAD
Libby, McNeill and Libby, Honolulu, T. H.
- C. E. MARSHALL
University of Missouri, Columbia, Missouri
- SANTE MATTSO
Lantbrukshögskolan, Uppsala, Sweden
- A. R. MIDGLEY
University of Vermont, Burlington, Vermont
- C. E. MILLAR
Michigan State College, East Lansing, Michigan
- C. A. MOOERS
University of Tennessee, Knoxville, Tennessee
- A. G. NORMAN
Camp Detrick, Frederick, Maryland
- MICHAEL PEECH
Cornell University, Ithaca, New York
- W. H. PIERRE
Iowa State College, Ames, Iowa
- ARTHUR L. PRINCE
Rutgers University, New Brunswick, New Jersey
- E. R. PURVIS
Rutgers University, New Brunswick, New Jersey
- L. A. RICHARDS
U. S. Regional Salinity Lab., Riverside, California
- C. O. ROST
University of Minnesota, St. Paul, Minnesota
- E. J. RUSSELL
Rothamsted Experimental Sta., Harpenden, Eng.
- OSWALD SCHREINER
Bureau of Plant Industry, Beltsville, Maryland
- JOHN W. SHIVE
Rutgers University, New Brunswick, New Jersey
- ROBERT L. STARKEY
Rutgers University, New Brunswick, New Jersey
- STEPHEN J. TOTH
Rutgers University, New Brunswick, New Jersey
- E. TRUOG
University of Wisconsin, Madison, Wisconsin
- S. C. VANDECAVEYE
State College of Washington, Pullman, Washington
- N. J. VOLK
Purdue University, Lafayette, Indiana
- SELMAN A. WAKSMAN
Rutgers University, New Brunswick, New Jersey
- S. WINOGRADSKY
Institut Pasteur, Paris, France

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879

Copyright, 1952, The Williams & Wilkins Company

CONTENTS

Liming the Soil	1
Plant Studies with Radioactive Calcium. DAVID RIRIE AND STEPHEN J. TOTH	1
Influence of Soil Acidity on Absorption of Calcium by Alfalfa as Revealed by Radio-calcium. W. R. SCHMEHL, MICHAEL PEECH, AND RICHARD BRADFIELD	11
Movement and Effect of Lime and Gypsum in Soil. DAVID RIRIE, STEPHEN J. TOTH, AND FIRMAN E. BEAR	23
Effect of Particle Size of Limestones on Soil Reaction, Exchangeable Cations, and Plant Growth. T. A. MEYER AND GARTH W. VOLK	37
A Method of Estimating the Reacting Rate of Different Particle Sizes of Limestone. R. P. THOMAS AND H. M. GROSS	53
Influence of Liming Materials on pH Values of Six Maryland Soils. J. H. HOYERT AND J. H. AXLEY	61
Influence of Placement of Lime Compounds on Root Development and Soil Characteristics. D. LONGENECKER AND F. G. MERKLE	71
Influence of Form, Fineness, and Amount of Limestone on Plant Development and Certain Soil Characteristics. R. L. BEACHER, D. LONGENECKER, AND F. G. MERKLE	75
A Nonstationary Method for Determining Thermal Conductivity of Soil in Situ. D. A. DE VRIES	83
Gaseous Diffusion and Porosity in Porous Media. C. H. M. VAN BAVEL	91
A Numerical Method for Solving the Flow Equation for Water in Unsaturated Materials. ARNOLD KLUTE	105
Phytase Activity in Soils. R. H. JACKMAN AND C. A. BLACK	117
Response of Crop Plants to I and Br. HARVEY P. NEWTON AND STEPHEN J. TOTH	127
The Aspergillus Niger Method for Determining Copper in Soils. MARJORIE WELSH DOLE	135
Effect of Fumigation on Some Chemical Properties of Soils. D. G. ALDRICH AND J. P. MARTIN	149
Books and News Note	161
✓ Hydrolysis of Phytate Phosphorus in Soils. R. H. JACKMAN AND C. A. BLACK	167
Effect of Organic Matter on Phosphate Availability. JOSEPH D. DALTON, GLENN C. RUSSELL, AND DALE H. SIELING	173
Some Characteristics of the Macrostructure of Tropical Soils in Puerto Rico. R. M. SMITH AND C. F. CERNUDA	183
Recovery of Fertilizer Nitrogen by Oats in the Greenhouse. W. V. BARTHOLOMEW AND A. E. HILTBOLD	193
Effect of Tillage Depth on Soil Conditions and Cotton Plant Growth for Two Alabama Soils. V. C. JAMISON, I. F. REED, C. M. STOKES, AND TOM E. CORLEY	203
Porous Tube Device for Sampling Soil Solutions During Water-Spreading Operations. RAY B. KRONE, H. F. LUDWIG, AND JEROME THOMAS	211
Freezing Point of Water in Puddled and Unpuddled Soils at Different Soil Moisture Tension Values. ROBERT B. CAMPBELL	221
Use of Total Yield for Predicting Nitrogen Content of Inoculated Legumes Grown in Sand Cultures. LEWIS W. ERDMAN AND URA MAE MEANS	231
Stability of DDT and Its Effect on Microbial Activities of Soil. L. W. JONES	237
Collection and Preservation of Soil Profiles. II. HENRY W. SMITH, R. A. MCCREERY, AND C. D. MOODIE	243
Books and News Note	249
Exchangeable Cation Analysis of Saline and Alkali Soils. C. A. BOWER, R. F. REITH-MEIER, AND M. FIREMAN	251
A Concept Concerning the Measurement of Available Soil Nutrients. MAURICE FRIED AND L. A. DEAN	263

Criteria for the Characterization of Kaolinite, Halloysite, and Related Mineral in Clays and Soils. LUIS BRAMAO, J. G. CADY, S. B. HENDRICKS, AND MAX SWERDLOW.	273
Use of Ca45 Labeled Calcium Carbonate in Determining Proportions of Native and Additive Calcium in Lysimeter Leachings and in Plant Uptake. HENRY C. HARRIS, W. H. MACINTIRE, C. L. COMAR, W. M. SHAW, S. H. WINTERBERG, AND S. L. HOOD.	289
Radiation Effects of Plants Grown in Soil Treated with Fertilizer Containing P32. JAMES M. BLUME.	299
✓ Uptake and Movement of Fertilizer Phosphorus. J. JORDAN, C. SIMKINS, G. COREY, R. KNIGHT, AND G. O. BAKER.	305
✓ Elongation of Seedlings as a Biological Test of Alkali Soils: I. Effects of Ions on Elongation. MOHAMED NAGUIB HASSAN AND ROY OVERSTREET.	315
Books.	327
Estimating the Integrated Soil Moisture Tension in the Root Zone of Growing Crops. STERLING A. TAYLOR.	331
Use of Dithizone As An Extractant to Estimate the Zinc Nutrient Status of Soils. ELLSWORTH SHAW AND L. A. DEAN.	341
Origin of the Base-Exchange Capacity of Clays and Significance of Its Upper Limiting Value. R. P. MITRA AND K. S. RAJAGOPALAN.	349
Effect of Iron and Aluminum Oxides on the Release of Calcium and on the Cation-Anion Exchange Properties of Soils. A. MEHLICH.	361
Accumulation of the Major Bases and Heavy Metals in Florida Citrus Soils in Relation to Phosphate Fertilization. WALTER REUTHER, PAUL F. SMITH, AND ALSTON W. SPECHT.	375
Leaching of Calcium in a Fine Sandy Loam As Indicated by Ca45. JAMES M. BLUME.	383
Determination of Soil Moisture by Neutron Scattering. WILFORD GARDNER AND DON KIRKHAM.	391
Ionization of Soils and Soil Colloids: III. Potassium-Calcium Relationships in Illite, Kaolinite, and Halloysite. S. A. BARBER AND C. E. MARSHALL.	403
Books and News Note.	415
Synthetic Soil Conditioners.	419
Influence of Organic Matter on Aeration and Structure of Soil. J. H. QUASTEL.	419
Effect of Synthetic Polyelectrolytes on Aggregation, Aeration, and Water Relationships of Soil. R. M. HEDRICK AND D. T. MOWRY.	427
✓ Effect of Synthetic Polyelectrolytes on the Structure of Saline and Alkali Soils. L. E. ALLISON.	443
Soil and Crop Responses from Field Applications of Soil Conditioners. W. P. MARTIN, G. S. TAYLOR, J. C. ENGIBOUS, AND E. BURNETT.	455
Effect of Synthetic Soil Conditioners on Erosion Control. LLOYD E. WEEKS AND WILLIAM G. COLTER.	473
Mechanism of Clay Aggregation by Polyelectrolytes. R. A. RUEHRWEIN AND D. W. WARD.	485
Index.	493

SOIL SCIENCE

VOLUME 73

January 1952

NUMBER 1

LIMING THE SOIL

For the last 5 years the National Lime Association has financed research fellowships at Pennsylvania State College and at Cornell, Ohio State, Maryland, and Rutgers Universities for the purpose of obtaining additional information on the effects of the various liming materials on acid soils and on plants growing on them. This issue of SOIL SCIENCE is devoted entirely to the reports on these and closely related studies. We are pleased to publish these papers for the benefit of the readers of the Journal. Material was also prepared for a popular bulletin, "One Hundred Questions and Answers on Liming Land," copies of which may be obtained by writing the Association, 925 15th St. N.W., Washington 5, D. C.

FIRMAN E. BEAR

PLANT STUDIES WITH RADIOACTIVE CALCIUM

DAVID RIRIE AND STEPHEN J. TOTH

New Jersey Agricultural Experiment Station¹

This study deals with the relative availability to plants of Ca in the carbonate phosphate, and sulfate forms, as applied to soil for correction of acidity and for fertilizing purposes. It also has to do with the translocation and distribution of Ca in various plants without reference to its source.

EXPERIMENTAL METHODS

A greenhouse pot experiment was conducted with Sassafra sandy loam. Radiocalcium (Ca45) was used at the rate of 47.3 μ c. a pot in tagging the salts. Glazed ceramic pots each containing 18 pounds of soil were treated with Ca salts as shown in table 1.

Potassium as KCl and Mg as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were added to each pot at the rate of 1.3 and 4.9 gm., respectively. B as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Cu as CuSO_4 , and Zn as ZnSO_4 , were also applied at the rate of 0.04 gm. of each salt. All salts, whether added in the dry state or in solution, were mixed thoroughly with the entire volume of soil. Optimum moisture was maintained in the soils by weighing the pots at 3-day intervals and adding distilled water.

Inoculated Ranger alfalfa seed was sown in the pots. The plants were thinned to four a pot on May 19, 1948. Tops were harvested June 26, July 27, and August 25, 1948. The tops were separated into upper and lower leaves and

¹ Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, the State University of New Jersey, department of soils.

stems. Roots were harvested after the third cutting and washed free of soil. Tops and roots were dried in a forced-air oven at 70°C. and analyzed.

The mineral content of the plants was determined by the method of Toth (9). Relative Ca45 activities of plant samples were estimated by the method of Reid (5). Total Ca was first determined on a digest of the plant fraction to be assayed. Aliquot portions of the digest were withdrawn to yield a standard weight of $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The Ca was precipitated in this form, collected on filter paper discs, washed with 95 per cent ethyl alcohol, and mounted in a brass ring assembly. The activities of the precipitates were determined by means of a G. M. tube of window thickness of 1.89 mgm./cm.² and a Tracer Auto-scaler.

The second phase involved a study of movement of Ca in plant roots. Rutgers tomato plants were seeded in sand in November 1949 and grown to a height of about 6 inches. In mid-December, selected plants were transplanted to specially

TABLE 1
Rate of application of Ca salts,* in study of Ca availability to plants

SERIES	CaCO ₃		Ca(H ₂ PO ₄) ₂ ·H ₂ O		CaSO ₄ ·2H ₂ O	
	Untagged	Tagged	Untagged	Tagged	Untagged	Tagged
1	15.9	0.5	1.7	—	0.85	—
2	16.4	—	0.2	1.5	0.85	—
3	16.4	—	1.7	—	—	0.85
4	16.4	—	1.7	—	0.85	—

* In grams a pot, containing 18 pounds soil.

arranged battery jars. The jars were set up in pairs, and the roots were split in such a manner that approximately half could be placed in each paired jar. All cultures were grown with forced aeration.

After being transplanted, the plants were grown in a standard nutrient solution until it was ascertained that all of them had survived the splitting of their roots and subsequent transplanting. The nutrient solution on which the plants were grown was a modification of that given by Shive and Robbins (6). It consisted of:

Salt.....	KH ₂ PO ₄	NaNO ₃	MgSO ₄ ·7H ₂ O	CaCl ₂
Molar concentration.....	0.0015	0.0040	0.0022	0.0024
B, 0.1 ppm.; Fe, 0.5 ppm.; Mn and Zn, 0.25 ppm. each.				

When the plants were in an early blossom stage, Ca⁴⁵Cl₂ was added² to one jar each of three sets of paired jars at the rate of 20 μc. The CaCl₂ plus Ca⁴⁵Cl₂ content of these jars totaled 0.0024 M. The CaCl₂ contents of the other jars of the pairs were 0, 0.0012 M, and 0.0024 M, respectively. The test was in duplicate.

Plants were allowed to grow in these solutions for 6 days without further

² Ca⁴⁵Cl₂ and Ca⁴⁵CO₃ used in this investigation were supplied by Oak Ridge Laboratory on authorization from the Isotopes Division, U. S. Atomic Energy Commission.

additions of nutrient solutions, except that distilled H_2O was added from time to time to maintain the volume. At the end of this period, the plants were harvested and sectioned, after which they were weighed, dried, and analyzed for Ca and Ca^{45} .

The third phase of the study involved preparation of radioautographs of old and young leaves of tomato, wheat, alfalfa, and red clover plants grown in soil under standard conditions to obtain information on distribution of Ca^{45} in the plants. Each pot of soil received 50 μ c. $Ca^{45}Cl_2$. Seventy-five days later, the leaves of the plants were harvested, pressed, dried, and exposed to Eastman No-Screen X-Ray Film for 30 days.

TABLE 2
Activities of various portions of alfalfa tops*

Ca SOURCE	TOP LEAVES			BOTTOM LEAVES		
	First Cutting	Second Cutting	Third Cutting	First Cutting	Second Cutting	Third Cutting
$Ca^{45}CO_3$	21,300	17,400	18,800	27,700	21,600	18,700
$Ca^{45}(H_2PO_4)_2 \cdot H_2O$	18,800	13,200	17,300	25,500	13,600	17,300
$Ca^{45}SO_4 \cdot 2H_2O$	20,600	9,300	16,900	24,100	11,100	17,800
	TOP STEMS			BOTTOM STEMS		
	First Cutting	Second Cutting	Third Cutting	First Cutting	Second Cutting	Third Cutting
$Ca^{45}CO_3$	9,600	8,400	9,300	6,900	7,200	7,700
$Ca^{45}(H_2PO_4)_2 \cdot H_2O$	7,600	6,500	7,700	5,700	5,100	7,300
$Ca^{45}SO_4 \cdot 2H_2O$	8,600	5,000	8,800	6,700	4,300	7,100

* Number of disintegrations a minute a gram of oven-dried tissue.

Leaves and stems of red clover were fractionated into stems, petioles ($\frac{1}{2}$ inch below pulvinus), midrib veins, complete leaves, outer leaf edges, and pulvini, and their Ca, Mg, and K contents were determined. Ca contents of upper and lower leaves of wheat and alfalfa were also determined.

Radioautographs of immature and mature leaves from a tomato plant grown in sand culture and receiving Ca^{45} for 6 days during the late growth stage were compared with those of mature leaves from a tomato plant grown in soil and receiving Ca^{45} continuously.

RESULTS AND DISCUSSION

Ca uptake from various Ca materials

Individual and total yields of three harvests of alfalfa tops and roots from the various Ca materials did not vary significantly and are not reported. Where Ca in the form of $CaCO_3$ was applied simultaneously with superphosphate, alfalfa absorbed more of it from the carbonate than from either the phosphate or sulfate form (tables 2, 3). This was indicated by the greater concentration of Ca^{45} in all plant fractions of the three harvests from series 1 (table 2). The

differences in Ca absorption from the three sources were reflected to a greater degree in the second than in the first or third harvests.

TABLE 3
Activities of the tops of three cuttings of alfalfa and of roots*

Ca SOURCE	TOPS			ROOTS
	First Cutting	Second Cutting	Third Cutting	
Ca45CO ₃	104,600	93,100	71,600	36,700
Ca45(H ₂ PO ₄) ₂ ·H ₂ O.....	98,100	61,400	61,500	22,000
Ca45SO ₄ ·2H ₂ O.....	96,100	60,200	64,000	26,400

* Number of disintegrations a minute for the total successive yields of alfalfa in each pot.

TABLE 4
Ca and K content of upper leaf portion of three harvests of alfalfa

Ca SOURCE	Ca			K		
	First Cutting	Second Cutting	Third Cutting	First Cutting	Second Cutting	Third Cutting
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Ca45CO ₃	2.10	1.75	1.98	2.83	2.77	3.13
Ca45(H ₂ PO ₄) ₂ ·H ₂ O.....	2.18	1.68	1.80	2.77	3.13	3.40
Ca45SO ₄ ·2H ₂ O.....	2.03	1.65	1.93	2.95	2.90	3.13
Control.....	2.00	1.68	2.00	2.65	2.87	3.37

TABLE 5
Activities of tomato plant fractions, half of roots immersed in nutrient solutions containing varying levels of Ca, and the other half in standard nutrient solutions containing Ca45*

PLANT FRACTION	JAR I— NO Ca45†	JAR II— Ca45†	JAR Ia— NO Ca45†	JAR IIa— Ca45†	JAR Ib— NO Ca45†	JAR IIb— Ca45†
Upper leaves.....	76,000	103,100	45,400	67,600	16,300	81,400
Lower leaves.....	39,900	132,700	58,200	157,100	23,100	103,400
Roots.....	50	66,200	0	79,700	0	68,400
Upper stems.....	N.D.§	78,000	N.D.§	52,900	N.D.§	58,800
Lower stems.....	N.D.§	78,900	N.D.§	100,700	N.D.§	72,300

* Number of disintegrations a minute a gram of oven-dried tissue.

† Jar I contained no Ca; jar Ia contained 0.0012 M CaCl₂; jar Ib contained 0.0024 M CaCl₂.

‡ Ca level equivalent to 0.0012 M CaCl₂ plus 0.0012 M Ca45Cl₂.

§ Not determined.

The distribution of Ca45 in the various portions of alfalfa tended to vary widely. The lower leaves contained more of it in eight out of nine instances than did the top leaves, but the top stem fractions contained more than the lower stems. The stem portions always contained less Ca45 than the leaves. The

relatively greater concentrations of Ca45 in the bottom leaves may be accounted for by immobilization of the cation following absorption.

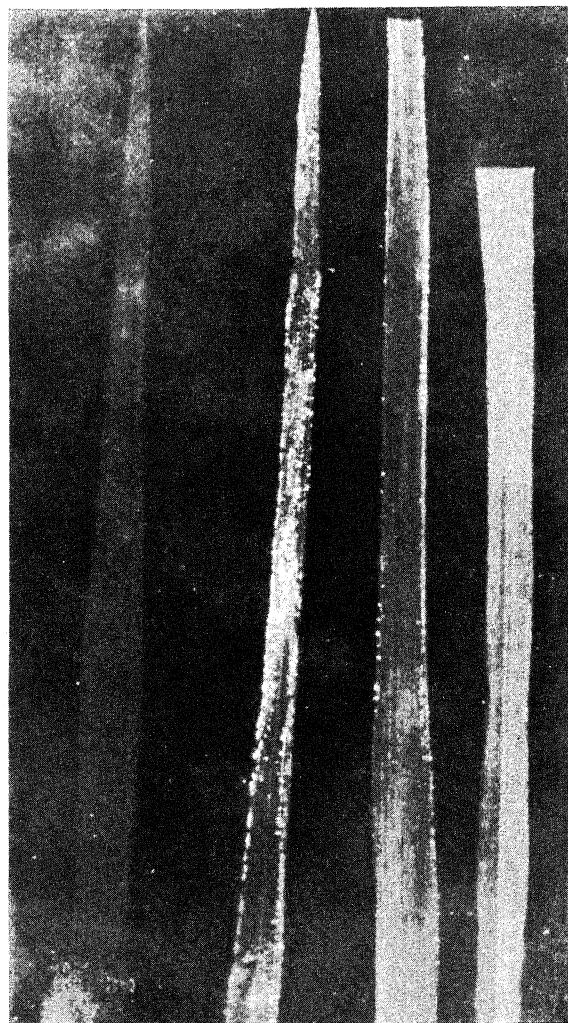


FIG. 1. RADIOAUTOGRAPH OF OLD (RIGHT) AND YOUNG (LEFT) WHEAT LEAVES CONTAINING Ca45

Note localization of Ca45.

Dosages of Ca45 applied to soils at rates equivalent to $47.3 \mu\text{c}$. did not affect Ca and K uptake by plants (table 4). Other major elements, data for which are not presented, were also unaffected.

The reason why Ca in the form of CaCO_3 is more available to alfalfa than is that in either the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ form when the salts are present as a mixture is not known. Fried and Peech (3) compared the effects of

lime and gypsum on plants, and found that plants grown on limed soils absorbed more Ca than those grown on gypsum-treated soils. This was true even though the soil solution of the gypsum-treated soil contained more Ca.

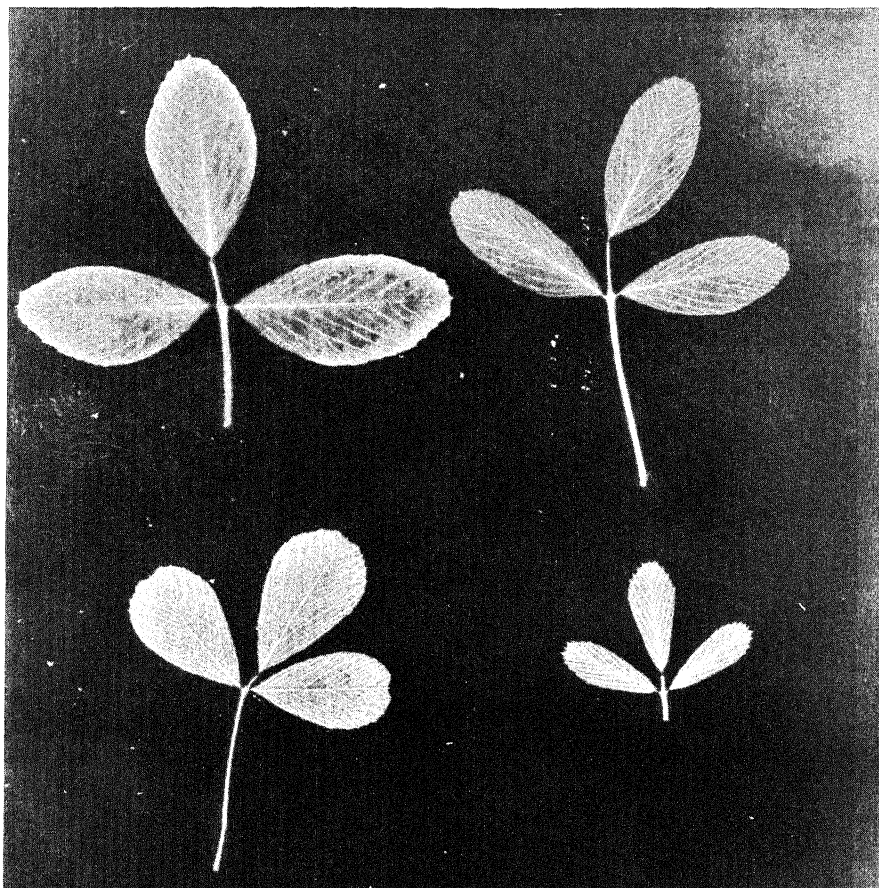


FIG. 2. RADIOAUTOGRAPH OF OLD (LEFT) AND YOUNG (RIGHT) ALFALFA LEAVES CONTAINING Ca45

Note absence of Ca45 in pulvini and concentration in veins and in older leaves.

Movement of Ca in tomato plants

Ca 45 was present in larger amounts in the side of the plant above the roots treated with radiocalcium than in the side above the roots receiving no radiocalcium (table 5). Leaves and branches from the side of the plant receiving Ca-45 contained more of the radioelement than those of the untreated side. The differences were variable, probably because of the difficulty of fractionation and also because of individual plant variations, and were not correlated with the Ca level in solution. The lower leaves appeared to concentrate Ca-45 more than did the top leaves.

Ca45 did not move from the roots treated with radiocalcium to those not so treated, except when Ca was completely omitted from solution, and then only a slight transfer occurred.

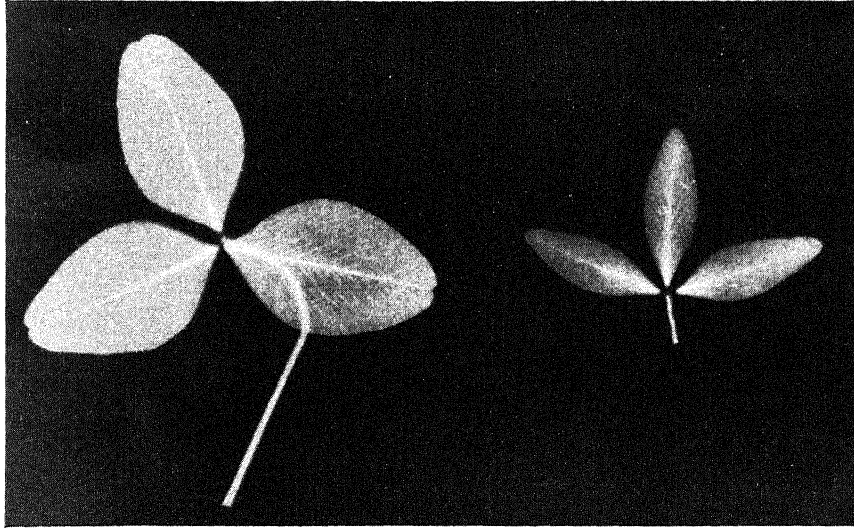


FIG. 3. RADIOAUTOGRAPH OF OLD (LEFT) AND YOUNG (RIGHT) RED CLOVER LEAVES
Note absence of Ca45 in pulvini and concentration in veins and in older leaf.

TABLE 6
Ca, K, and Mg contents of red clover fractions

PLANT SECTION	Ca	K	Mg
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Stems.....	2.26	1.33	0.14
Petioles ($\frac{1}{2}$ inch below pulvinus).....	3.12	2.45	0.65
Midrib veins.....	3.71	1.14	0.42
Outer leaves.....	3.40	0.94	0.43
Leaves (whole).....	3.53	1.05	0.43
Pulvini.....	1.42	2.38	0.52

Radioautographs and assays of Ca45 in plants

The patterns of Ca45 distribution in wheat, alfalfa, and red clover plants are shown by figures 1, 2, and 3.

In all three plants, more Ca45 was present in the old than in the young leaves. The leaf veins of alfalfa and red clover contained more Ca45 than did the leaf edges. Localized concentrations of Ca45 were also observed in the older leaves of wheat and alfalfa, possibly because of cell inclusions of insoluble crystals. Insoluble Ca compounds of various types have been reported to occur in plants (1, 2, 4, 7, 8).

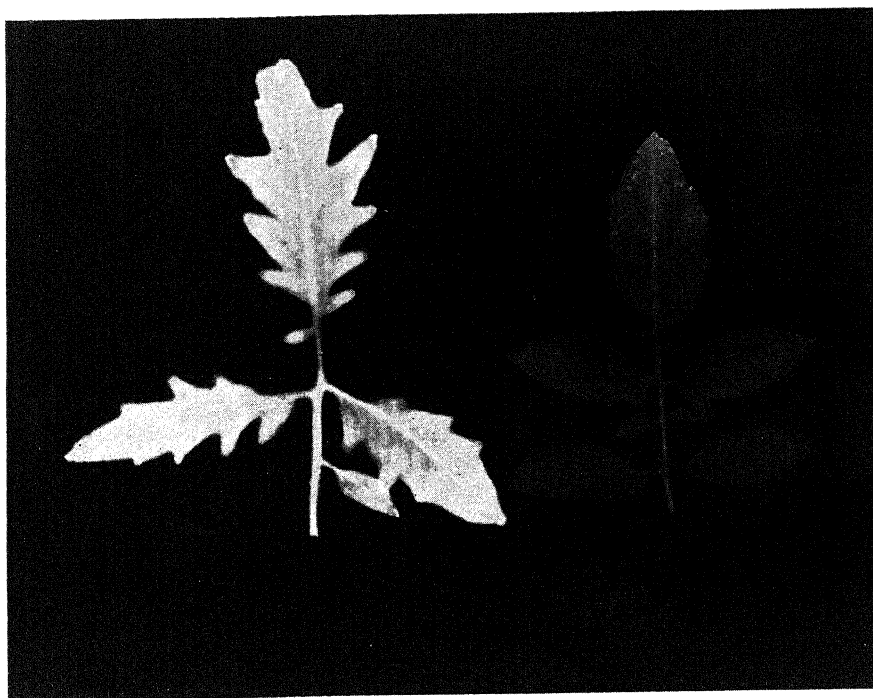


FIG. 4. RADIOAUTOGRAPH OF OLD (LEFT) AND YOUNG (RIGHT) TOMATO LEAVES TREATED CONTINUOUSLY WITH Ca^{45}

Note higher concentration of Ca^{45} in older leaf at left.

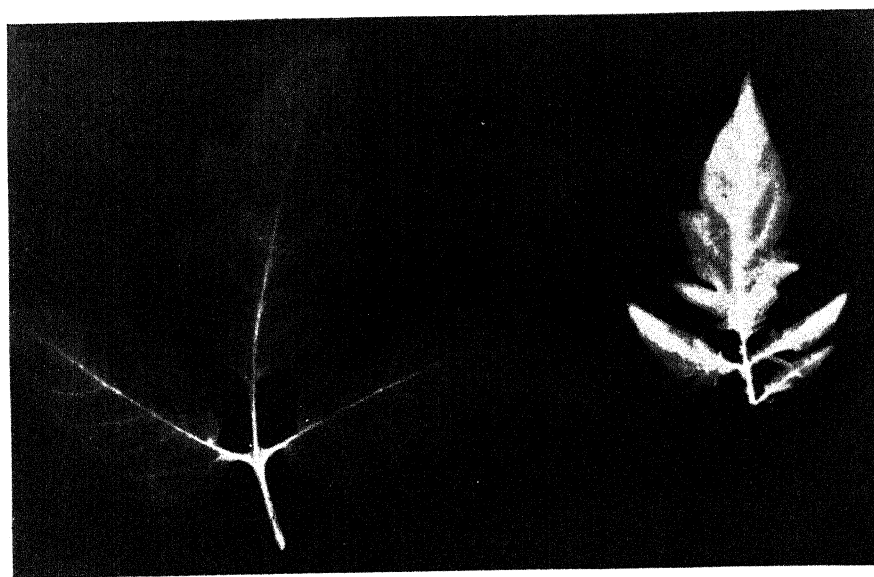


FIG. 5. RADIOAUTOGRAPH OF OLD (LEFT) AND YOUNG (RIGHT) TOMATO LEAVES TREATED FOR 6 DAYS WITH Ca^{45}

Note higher concentration of Ca^{45} in younger leaf at right.

The pulvini³ of alfalfa and red clover leaves and the points of leaf attachment to the petiole and of the petiole to the stem were notably lacking in Ca45. Meyer and Anderson (4) describe the pulvinus cells as relatively large, thin-walled compact groups. The thin walls are quite possibly associated with low Ca content. Such cells are involved in the movements of legumes, occurring when the leaves are exposed to such stimuli as light, electricity, or treatment with chemicals.

Detailed chemical studies showed that the pulvini and other sections of red clover are low in Ca, high in K, and slightly higher in Mg than leaves or stems (table 6). The section of petiole immediately adjacent to the pulvinus is lower in Ca but slightly higher in K and Mg than are the leaves.

Figure 4 shows a radioautograph of old and young tomato leaves grown continuously with Ca45, and figure 5 shows those subjected to a 6-day treatment with the radioelement. When the plant was grown continuously with Ca45, the radioelement tended to concentrate in the older leaves; in the plant treated for only 6 days, the Ca45 tended to concentrate in the young leaves. Apparently, one can arrive at erroneous conclusions concerning absorption and translocation of Ca45 in plants unless the details of procedure are clearly stated.

In all studies with Ca45, whether in solution, sand, or soil cultures, no apparent radiation injury to the plants was observed.

SUMMARY AND CONCLUSIONS

Plant studies were conducted to determine the relative availability to tomato plant of Ca45 from a mixture of three tagged Ca salts, its movement within the tomato plant, and its distribution within leaves of tomato, alfalfa, red clover, and wheat plants.

The most important findings were:

Ca45 from Ca45CO_3 was more available to alfalfa than that from $\text{Ca45}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{Ca45SO}_4 \cdot 2\text{H}_2\text{O}$.

Greater amounts of Ca45 were present in the lower than in the upper leaves of plants, but more was present in the upper than in the lower stems.

Ca45 had no apparent effect on the uptake of other mineral nutrients by alfalfa.

Split root studies with tomatoes indicated little transfer of Ca45 from roots immersed in solutions containing Ca45 to those of the same plant immersed in standard nutrient solutions containing varying levels of Ca.

Radioautographs of wheat and alfalfa showed localized concentrations of Ca45 in the outer edges of older leaves.

Ca45 seemed to be concentrated to a greater degree in the veins than in the other parts of the leaf of alfalfa and red clover.

The pulvini of alfalfa and red clover were notably low in Ca45.

Analyses of red clover pulvini showed relatively low Ca contents and relatively high K and Mg contents, in comparison with other plant fractions.

Older leaves contained more Ca45 than did younger leaves when plants were

³ These findings are the basis of the observations of Stewart and Bear on absence of Ca in the pulvini of ladino clover published in N. J. Agricultural Experiment Station Bulletin 759.

grown on a continuous source of the radioelement. When Ca^{45} was applied to tomato plants at a late growth stage, it concentrated in the younger leaves.

REFERENCES

- (1) ASENJO, C. E., GOYCO, J. A., AND FERNANDEZ, M. D. C. 1944 A note on the presence of calcium oxalate in the Maya fruit. *Jour. Amer. Pharm. Assoc., Sci. Ed.* 33 (10): 344-345.
- (2) CHANDLER, R. F., JR. 1937 Certain relationships between calcium and oxalate content of foliage of certain forest trees. *Jour. Agr. Res.* 55: 393-398.
- (3) FRIED, M., AND PEECH, M. 1946 Comparative effects of lime and gypsum upon plants grown on acid soils. *Jour. Amer. Soc. Agron.* 38: 614-623.
- (4) MEYER, B. S., AND ANDERSON, D. B. 1939 *Plant Physiology*. D. Van Nostrand and Co., Inc., New York.
- (5) REID, A. F. 1947 *Preparation and Measurement of Isotopic Tracers*. J. W. Edwards, Ann Arbor, Michigan.
- (6) SHIVE, J. W., AND ROBBINS, W. R. 1948 *Methods of growing plants in solution and sand cultures*. N. J. Agr. Exp. Sta. Bul. 636.
- (7) SWANBACK, T. R. 1938 Variations in chemical composition of leaves (of tobacco) according to position on the stalk. *Conn. Agr. Exp. Sta. Bul.* 42: 22-36.
- (8) THODAY, D., AND EVANS, H. 1932 *Studies in growth and differentiation: II*. *Ann. Bot.* 46: 781-807.
- (9) TOTH, S. J., et al. 1948 Rapid quantitative determination of eight mineral elements in plant tissue by a systematic procedure involving use of a flame photometer. *Soil Sci.* 66: 459-466.

INFLUENCE OF SOIL ACIDITY ON ABSORPTION OF CALCIUM BY ALFALFA AS REVEALED BY RADIOCALCIUM

W. R. SCHMEHL, MICHAEL PEECH, AND RICHARD BRADFIELD

Cornell University¹

The response of plants, especially legumes, to application of lime on acid soils has usually been attributed to the increased supply of nutrient calcium, even though many acid soils may contain as much as 2,000 pounds of Ca per acre-6-inches. Recent studies at this institution (3, 11) have shown that the poor growth of plants on acid soils is not necessarily due to Ca deficiency in the soil or within the plant. Nevertheless, the growth and the Ca content of the plants are both markedly increased by liming an acid soil, whereas applications of gypsum, which is much more soluble than CaCO_3 at the partial pressures of CO_2 encountered in the soil air, not only fail to increase growth but also frequently fail to increase the Ca content of the plants grown on acid soils. This would suggest that some factor other than the low available Ca supply may reduce the uptake of Ca by plants under acid soil conditions. In the studies reported in this paper, use has been made of radiocalcium² to determine the influence of H^+ , Mn^{++} , and Al^{+++} on the absorption of Ca^{++} by alfalfa grown in soils as well as in nutrient solutions.

EXPERIMENT I: EFFECT OF RATE AND METHOD OF LIMING

If the main function of liming an acid soil is to increase Ca as a plant nutrient, the method of applying limestone that effects the greatest uptake of Ca by plants should produce the highest yield. The object of Experiment I was to determine the utilization by alfalfa of Ca from radioactive CaCO_3 applied to an acid soil at varying rates.

Materials and methods

The experiment was conducted in rectangular glazed earthenware containers 16 by 18½ inches in cross-sectional area, 17 inches deep, and provided with a drainage hole. A 1-inch layer of quartz sand was spread on the bottom of each container before it was filled with 207 pounds moist soil containing 12 per cent water. The soil used in this study was Mardin silt loam taken from the A_p horizon of an abandoned area on the Mount Pleasant Experimental Farm, Ithaca, New York. Initially the soil contained, per 2,000,000 pounds, 650 pounds exchangeable Ca as determined by the ammonium acetate method (9) and 300 pounds Al, 38 pounds Fe, 60 pounds Mn, 5 pounds P, 50 pounds Mg, and 165 pounds K as determined by rapid microchemical soil tests (8). The pH of the soil was 4.8. The soil was mixed with the reagent grade $\text{NH}_4\text{H}_2\text{PO}_4$, KNO_3 ,

¹ Contribution from the department of agronomy, Cornell University, Ithaca, N. Y.

² Radiocalcium, in the form of irradiated CaCO_3 , was supplied by the U. S. Atomic Energy Commission.

K_2SO_4 , $MgCO_3$, and $Na_2B_4O_7 \cdot 10H_2O$ to supply the equivalent of 200 pounds P_2O_5 , 200 pounds K, 32 pounds N, 100 pounds Mg, and 2.5 pounds B per 2,000,000 pounds.

The four liming treatments, replicated twice, are shown in table 1. In the first three treatments, the 0-3½-inch layer (25 per cent of the total soil volume) was limed at rates of 2, 4, and 8 tons $CaCO_3$ per 2,000,000 pounds of soil; in the fourth treatment, the soil was limed throughout the entire depth at the rate of 4 tons $CaCO_3$ per 2,000,000 pounds. Radioactive $CaCO_3$, containing 0.5 μ c. Ca^{45} per gram $CaCO_3$ and prepared by precipitation from a $CaCl_2$ solution, was used to lime the 0-3½-inch layer in all treatments.

Ontario variegated alfalfa was seeded on July 7, 1947, and after several weeks the plants were thinned to 75 per container. Optimum moisture was maintained

TABLE 1
Plan of Experiment I; effect of rate and method of liming on yield and calcium content of alfalfa

TREATMENT NUMBER	RATE OF LIMING		DEPTH OF LIMING	DEPTH TO WHICH LABELED $CaCO_3$ WAS INCORPO- RATED	pH OF LIMED SOIL	AVERAGE YIELD PER CUTTING	Ca CONTENT (AVERAGE OF THREE CUTTINGS)
	Per acre (area basis)	Per 2,000,000 pounds soil in limed layer					
	lb.	lb.	in.	in.		gm./pot	per cent
1	2,000	4,000	0-3½	0-3½	5.8	47.8**	2.55
2	4,000	8,000	0-3½	0-3½	6.6	48.9**	2.82
3	8,000	16,000	0-3½	0-3½	7.6	52.7*	2.79
4	16,000	8,000	0-14	0-3½	6.6	60.4	2.97
L.S.D. (0.05)						7.5	N.S.
L.S.D. (0.01)						10.6	

* Yield less than treatment 4 at 5 per cent level.

** Yield less than treatment 4 at 1 per cent level.

by subirrigation and by occasional surface irrigation with distilled water. Artificial lights were used during late fall and winter. Good growth of alfalfa was obtained through October, but thereafter growth was somewhat reduced because of inadequate lighting. Three cuttings of alfalfa were made in the early blossom stage on October 27 and December 12, 1947, and on January 19, 1948. The plant material was dried at 70°C.; the leaflets and petioles were separated and saved for chemical analysis. After the third cutting, the roots from one replication of each treatment were removed separately from the 0-3½- and the 3½-14-inch layers, washed, dried, and saved for chemical analysis.

The radioactivity of Ca in the plant material was determined by counting from the calcium oxalate precipitate collected on disks of filter paper by means of a filtering assembly similar to that described by MacKenzie and Dean (7). Corrections for self-absorption were made by the method described by Henriques *et al.* (4) for S35. Total Ca in the same precipitate was determined gravimetrically.

The proportion of the Ca in the plants derived from the radioactive $CaCO_3$

was calculated from the ratio $S_{\text{plants}}/S_{\text{CaCO}_3}$, in which S_{plants} and S_{CaCO_3} refer to the specific activity of the Ca in the plant material and in the applied CaCO_3 respectively. The proportion of the Ca in the plants derived from the 0-3½-inch layer of soil was also calculated from the ratio $S_{\text{plants}}/S_{\text{exch. Ca}}$, in which $S_{\text{exch. Ca}}$ is the specific activity of the exchangeable Ca in the 0-3½-inch layer. The latter calculation was possible because the added CaCO_3 had reacted with the soil at the start of the experiment and was in isotopic equilibrium with the exchangeable Ca.

Results and discussion

The yields and the Ca content of alfalfa in Experiment I are shown in table 1. When only the 0-3½-inch layer of soil was limed, the rate of liming had little

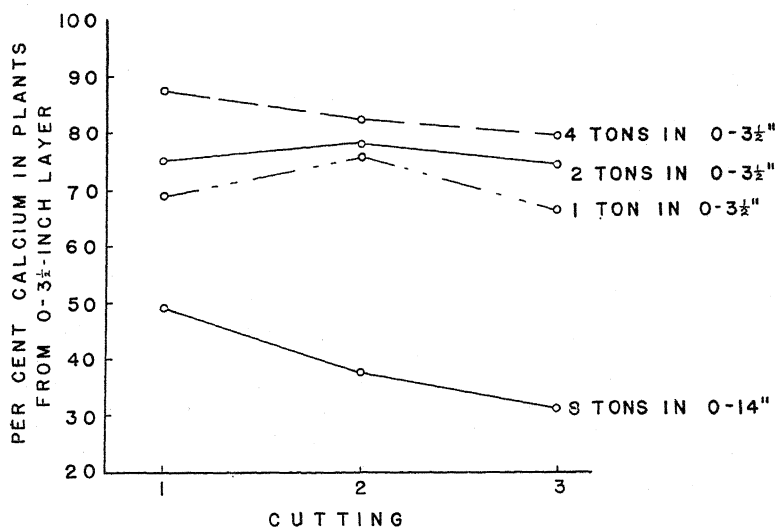


FIG. 1. PROPORTION OF THE Ca IN ALFALFA DERIVED FROM THE 0-3½-INCH LAYER OF SOIL, EXPERIMENT I

influence on the yield of alfalfa, but the yield was significantly increased when the entire volume of soil was limed (treatment 4). The Ca content of the plants did not differ greatly between treatments; this would indicate that the Ca content was not limiting growth.

As shown in figure 1, the proportion of the Ca in the plants derived from the 0-3½-inch layer of soil when the entire volume of soil was limed (treatment 4) was much less than that when only the surface soil was limed. About 80 per cent of the Ca in the plants was derived from the limed layer when only the 0-3½-inch layer of soil was limed. Inasmuch as the soil in the fourth treatment was uniformly limed, the results of Ca uptake from the 0-3½-inch layer make possible the estimation of the relative distribution of roots effective in the absorption of Ca. It will be noted that 50 per cent of the Ca in the plants was derived from the 0-3½-inch layer at the first cutting; as roots penetrated to

greater depths, the proportion of the Ca in the plants derived from this layer decreased to 27 per cent for the third cutting.

Roots removed from the 0-3½- and 3½-14-inch layers of soil were analyzed for total and radioactive Ca. The results are recorded in table 2. The presence of Ca45 in the roots removed from the 3½-14-inch layer may be attributed to down-

TABLE 2
Ca content of alfalfa roots, Experiment I

TREATMENT NUMBER	Ca CONTENT OF ROOTS IN THE TWO LAYERS		PROPORTION OF Ca IN ROOTS DERIVED FROM LABELED CaCO ₃ *	
	0-3½ in.	3½-14 in.	0-3½ in.	3½-14 in.
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	0.26	0.20	39.9	2.2
2	0.30	0.23	53.6	11.8
3	0.32	0.26	66.9	27.8
4	0.37	0.40	29.6	1.8

* Labeled CaCO₃ applied in the 0-3½-inch layer of soil.

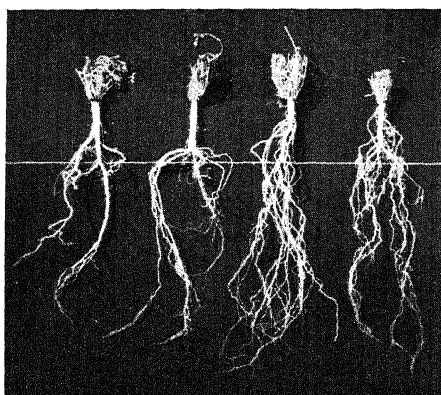


FIG. 2

FIG. 2. ROOTS REMOVED FROM TREATMENT 2, EXPERIMENT I

The 0-3½-inch layer was limed to pH 6.6; the 3½-14-inch layer was at pH 4.8. The white line represents a depth of 3½ inches.

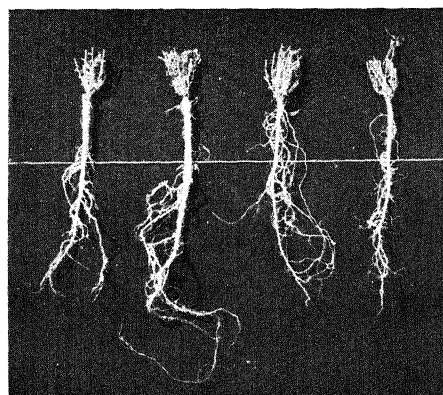


FIG. 3

FIG. 3. ROOTS REMOVED FROM TREATMENT 4, EXPERIMENT I

The total soil volume (0-14 inches) was limed to pH 6.6. The white line represents a depth of 3½ inches.

ward translocation of Ca within the roots, because examination of the soil from this layer showed no appreciable leaching of Ca. The Ca content of the roots was much lower than that of the leaflets or petioles. The Ca content of the roots from the limed layer was generally higher than that from the corresponding unlimed layer, but the Ca content of the roots from both soil layers was highest when the entire soil was limed. When the subsoil was not limed, 40 to 67 per cent of the Ca in roots from the 0-3½-layer was derived from labeled CaCO₃.

applied in the same layer. As much as 28 per cent of the Ca in the roots from the 3½-14-inch layer was derived from the Ca applied to the 0-3½-inch layer. There was, therefore, considerable downward movement of Ca within the roots when the 0-3½-layer of soil was heavily limed; this was also reflected by a slight increase in the Ca content of the roots from the unlimed layer as the rate of liming in the surface layer was increased. There was little downward movement of Ca into the roots in the 3½-14-inch layer with the lowest rate of liming (treatment 1); nor was there much downward movement of Ca in the roots when the whole soil was limed.

TABLE 3

Plan of Experiment II, and average yield and Ca content of four cuttings of alfalfa

TREATMENT	pH		LAYER IN WHICH Ca WAS LABELED	AVERAGE YIELD PER CUTTING	Ca CONTENT (AVERAGE OF FOUR CUTTINGS)
	0-2 in.	2-10 in.			
			<i>inch</i>	<i>gm./pot</i>	<i>per cent</i>
1. Control†.....	4.8	4.8	—	5.72	2.08
2. 570 lb. per acre applied with seed.	4.8	4.8	‡	7.11*	2.20
3. 0-2-inch layer limed and diluted with sand.....	6.5	4.8	0-2	8.79**	2.03
4. 2-10-inch layer limed and diluted with sand.....	4.8	6.5	2-10	7.40**	2.19
5. 0-10-inch layer limed and diluted with sand.....	6.5	6.5	0-2	9.16**	2.69**
6. Acid-leached soil limed to pH 4.8..	4.8	4.8	0-10	5.88	2.09
L.S.D. (0.05).....				1.09	0.27
L.S.D. (0.01).....				1.48	0.38

† The original soil in treatments 1 to 5 inclusive contained 1.6 me. Ca per 100 gm. soil. In treatments 3, 4, and 5, the limed layer (pH 6.5) was diluted with sand to make the exchangeable Ca content per unit volume of diluted soil the same as that of the original acid soil. In treatment 2 an additional amount, 570 pounds CaCO₃ per acre (area basis), was localized with the seed. The soil in treatment 6 contained 3.2 me. Ca per 100 gm. soil after liming.

‡ In CaCO₃ applied with seed.

* Greater than the control at the 5 per cent level.

** Greater than the control at the 1 per cent level.

When the roots were removed for analysis, the taproots in treatment 4 were longer than those in other treatments. When only the surface soil was limed, more lateral roots developed in the limed soil immediately above the unlimed subsoil. The abnormal root development in treatment 2 is shown in figure 2; taproots typical of those found in treatment 4 are shown in figure 3. Poor root development by legumes grown in strongly acid soils has been observed by other investigators (2, 10, 14).

EXPERIMENT II: EFFECT OF SOIL pH WITH CONSTANT EXCHANGEABLE CALCIUM

A second experiment was conducted to determine the influence of soil reaction on the uptake of Ca by alfalfa when the total exchangeable Ca per unit volume

was kept constant. The absorption of Ca by alfalfa from CaCO_3 placed with the seed was also determined.

Materials and methods

The plan of this experiment is shown in table 3. Mardin silt loam from the Mount Pleasant Farm was again used here for treatments 1 to 5 inclusive. The soil for treatment 6 was obtained from an adjacent area that had been treated with sulfur in 1942 at the rate of 1 ton per acre. After being limed to pH value of 4.8, the soil in treatment 6 contained 3.2 me. of Ca per 100 gm.

The original soil in treatments 1 to 5 inclusive contained 1.6 me. Ca per 100 gm. soil. In treatments 3, 4, and 5, the limed soil (pH 6.5) was diluted with quartz sand to make the exchangeable Ca content per unit volume of diluted soil the same as that of the original acid soil. In treatment 2, CaCO_3 labeled with Ca45 was applied with the seed at a depth of about $\frac{1}{2}$ inch. A parallel treatment (not shown in the plan of the experiment, table 3) in which nonradioactive CaCO_3 was placed with the seed showed that the level of Ca45 activity used in this experiment (0.45 μc . Ca45 per gram of CaCO_3) was not injurious to the germination or subsequent growth of alfalfa. In treatment 6, labeled CaCO_3 was used to increase the pH of the acid-leached Mardin soil from 4.0 to 4.8. All treatments received N, P, K, Mg, and B at the same rates as in Experiment I.

The soil was placed in 3-gallon glazed pots and seeded, on July 27, 1947, to Ontario variegated alfalfa. Each treatment was duplicated. Distilled water was added frequently to maintain moisture content equivalent to 30 per cent of the weight of the soil plus 15 per cent of the weight of the sand. The seedlings were thinned on August 19 and 27 to a final stand of 13 plants per pot. The alfalfa was cut in the early blossom stage on October 16, November 14, and December 17, 1947, and on January 19, 1948. The plant material was dried at 70°C. and weighed. The leaflets and petioles were separated for the determination of total Ca and Ca45. Manganese-toxicity symptoms, described previously (11), were noted on plants from treatments 1, 2, and 6.

Results and discussion

The average yield and the Ca content of the plants are listed in table 3. When the entire volume of soil was maintained at pH 6.5 (treatment 5), the Ca content of the plants exceeded that in other treatments, which had little effect on the Ca content of the alfalfa. The highest yields of alfalfa were obtained when the soil in the 0-2-inch layer was at pH 6.5 (treatments 3 and 5). Growth of alfalfa on the unlimed Mardin soil (treatment 1) was as good as that on the acid-leached Mardin soil limed to pH 4.8 but containing twice as much exchangeable Ca. Thus, soil reaction and associated factors had a greater influence than the Ca level in controlling the growth of alfalfa on the Mardin soil. This confirms the results of previous studies with the same soil (11).

The yield produced by the localized application of CaCO_3 with the seed (treatment 2) was higher than that of the control but lower than those obtained when the surface 2 inches of soil was maintained at pH 6.5 without increasing

the exchangeable Ca. Field trials at this institution on a strongly acid Mardin soil have shown that a 1,000-pound application of limestone localized with the seed increased the yield of alfalfa; but this treatment was inferior to that in which 4 tons of limestone was mixed with the soil to a depth of 6 or more inches.

The percentage of Ca in plants derived from the layer in which the exchangeable Ca was labeled is shown in table 4. Because the lime applied in treatment 2 was localized with the seed, the figures for this treatment show the percentage of Ca in plants derived from this labeled CaCO_3 . From the data in table 4, it is possible to compare the uptake of Ca from the two layers, 0-2 inches and 2-10 inches, in which the exchangeable Ca content was kept constant at pH values

TABLE 4
Influence of soil reaction on absorption of Ca by alfalfa, Experiment II

TREATMENT NUMBER	LAYER IN WHICH EXCHANGEABLE Ca WAS LABELED	PROPORTION OF Ca IN PLANTS DERIVED FROM LAYER IN WHICH EXCHANGEABLE Ca WAS LABELED					
		Seedling stage		Cutting			
		23 days	31 days	1	2	3	4
	inch	per cent	per cent	per cent	per cent	per cent	per cent
2	*	29.8	17.7	10.4	20.3	19.0	16.3
3	0-2	67.2	55.3	34.2	43.3	42.9	24.4
4	2-10	61.4	73.6	75.8	81.1	75.9	81.3
	{ 0-2]†	[38.6]	[26.4]	[24.2]	[18.9]	[24.1]	[18.7]
5	0-2	33.6	13.6	22.7	30.3	23.1	17.0
6	0-10	98.7	100.6	96.7	98.8	98.8	97.6

* In labeled CaCO_3 applied with seed; the figures shown for treatment 2 represent the percentage of Ca in plants derived from this labeled CaCO_3 .

† The bracketed figures for treatment 4 show the percentage of Ca in plants derived from the exchangeable Ca in the 0-2-inch layer, and were obtained by subtracting from 100 the percentage of Ca in plants derived from the 2-10-inch layer.

4.8 and 6.5. The largest proportion of Ca in plants was taken up from the 0-2-inch layer only when this layer was maintained at pH 6.5. Comparison of treatments 4 and 5 shows that approximately the same proportion of Ca in plants was absorbed from the 0-2-inch layer at both pH values when the 2-10-inch layer was maintained at pH 6.5. Treatments 3 and 5 afford a comparison of the uptake of Ca from the 2-10-inch layer at the two pH values when the pH value of the 0-2-inch layer was maintained at 6.5. The proportion of Ca in plants derived from the 2-10-inch layer may be obtained by subtracting from 100 the percentage of Ca in plants derived from the 0-2-inch layer listed in table 4. In contrast to the same uptake of Ca from the 0-2-inch layer at both pH values when the 2-10-inch layer was maintained at pH 6.5, the proportion of the Ca in the plants derived from the lower layer at pH 6.5 was greater than that at pH 4.8 when the pH of the upper layer was maintained at pH 6.5. In light of the abnormal development of the taproots in the acid subsoil, observed in Experiment I, it is difficult to determine to what extent the relative uptake of Ca from the two layers may have been influenced by the different root distribution

found in the acid 2-10-inch layer. The data of this experiment, however, show that the absorption of Ca by the roots from the 2-10-inch layer was decreased at the lower pH value.

When CaCO_3 was placed with the seed (treatment 2), 30 per cent of the Ca in the seedlings, after 23 days, was derived from the applied lime. With increasing penetration of the roots into the soil, the proportion decreased to 10 per cent for the first cutting, but then increased again to about 20 per cent for the subsequent cuttings.

The soil in treatment 6 was limed uniformly with labeled CaCO_3 . Because of isotopic exchange equilibrium, the specific activity (counts per minute per unit weight of Ca) of Ca in the plants remained constant throughout the experiment and was found to be equal to the specific activity of the exchangeable Ca. The specific activity of the exchangeable Ca determined after extraction with neutral normal ammonium acetate agreed with that calculated by assuming complete equilibrium of the added (labeled) Ca with the exchangeable Ca in the soil.

EXPERIMENT III: EFFECT OF MANGANESE, ALUMINUM, AND HYDROGEN IONS

Hewitt (5) and others (6, 12) have noted that high concentration of Al^{+++} or Mn^{++} may reduce the uptake of calcium by plants. Arnon *et al.* (1) found that high H^+ concentration would reduce the absorption of calcium by lettuce. The object of Experiment III was to determine the direct effect of Mn^{++} , Al^{+++} , and H^+ in nutrient solution on the absorption of calcium by alfalfa. Radiocalcium was used for this purpose in short-time absorption experiments to eliminate the complex growth-composition interaction.

Materials and methods

One week after germination in quartz sand, seedlings of Ontario variegated alfalfa were transferred to 3-gallon crocks containing complete nutrient solution. The seedlings were supported in Pyrex glass tubes inserted through 2-inch cork stoppers. Eight cork stoppers, each holding four seedlings, were held in each galvanized crock cover. This plant culture technique was similar to that described by Wallihan (13). The level of the nutrient solution was maintained in contact with the lower end of the glass tube until the roots were 3 to 4 inches long; thereafter, the level of the solution was kept about an inch lower. Equally satisfactory growth was obtained with and without aeration. The basic nutrient solution for growing the seedlings prior to treatment was essentially the same as that used by Arnon *et al.* (1). For series 1 the composition was: 0.0015 *M* $\text{Ca}(\text{NO}_3)_2$, 0.005 *M* KNO_3 , 0.001 *M* MgSO_4 , 0.001 *M* $\text{NH}_4\text{H}_2\text{PO}_4$, 0.5 ppm. B, 0.1 ppm. Mn, 0.05 ppm. Zn, and 0.02 ppm. Cu, and with 7 ml. 9.5 per cent ferric tartrate per 3-gallon crock every 3 days. Half of this concentration was used as the basic nutrient solution for series 2.

The influence of Al-, Mn-, and H-ion concentrations on Ca absorption was determined by transferring plants grown in the basic nutrient solution into nutrient solutions containing Ca^{45} with varying Al-, Mn-, and H-ion concentrations. After absorption periods of 35 or 36 hours, the tops were harvested

and analyzed for Ca45; the specific activity of the Ca in the tops was used as a measure of the relative uptake of Ca. It may be of interest to note here that in a preliminary experiment to determine the rate of absorption of Ca by plants during a 24-hour period, it was found that no absorption of Ca took place during the night in absence of light.

Series 1. The alfalfa plants, 3 and 3½ weeks old (groups B and A respectively), were transferred from the basic nutrient solution into the following solution common to all treatments: 0.00125 M Ca(NO₃)₂, 0.001 M MgSO₄, 0.002 M

TABLE 5

Influence of Al⁺⁺⁺ and Mn⁺⁺ concentration in nutrient solutions on the absorption of calcium by alfalfa, series 1, Experiment III

TREATMENT*	SPECIFIC ACTIVITY OF Ca IN TOPS†	
	Group A	Group B
Control	242	554
10 ppm. Mn	158	486
100 ppm. Mn	196	336
10 ppm. Al	25.7	62.3
100 ppm. Al	1.9	5.0

* Absorption time—35 hours.

† Counts per minute per milligram precipitate corrected for resolving time, background, and self-absorption.

TABLE 6

Influence of the H⁺ concentration in nutrient solutions on absorption of calcium by alfalfa, series 2, Experiment III

TREATMENT*	SPECIFIC ACTIVITY OF Ca IN TOPS†	
	Group A	Group B
pH 4.5	1035	506
pH 5.5	1118	645
pH 6.5	1170	765

* Absorption time—36 hours.

† Counts per minute per milligram calcium oxalate, corrected for resolving time, background, and self-absorption.

KNO₃, 0.001 M NH₄NO₃, 0.1 ppm. Mn, and 0.1 ppm. B. Calcium was supplied by radioactive Ca(NO₃)₂ that contained 8 µc. Ca45 per gram Ca. Manganese or Al was added at varying concentrations to give the following treatments: 1, control; 2, 10 ppm. Mn; 3, 100 ppm. Mn; 4, 10 ppm. Al; and 5, 100 ppm. Al. The pH of all treatments was maintained between 4.2 and 4.3 by frequent adjustment with NaOH or HCl. Eight plants were harvested for analysis after a 35-hour absorption period.

Series 2. The influence of the H-ion concentration on Ca absorption was determined by transferring plants 2½ and 3 weeks old (groups A and B respectively) into nutrient solutions at pH 4.5, 5.5, and 6.5. The pH was kept within

± 0.1 unit by frequent adjustment with NaOH or HCl. The nutrient solution used for series 2 had the following composition: 0.00125 *M* $\text{Ca}(\text{NO}_3)_2$, 0.002 *M* KNO_3 , 0.001 *M* MgSO_4 , 0.1 ppm. B, 0.005 per cent ferric citrate. The specific activity of $\text{Ca}(\text{NO}_3)_2$ was the same as that of the $\text{Ca}(\text{NO}_3)_2$ used in series 1. Each treatment was duplicated. Sixteen plants from group A and eight from group B were taken for each analysis after a 36-hour absorption period.

Results and discussion

The uptake of Ca by alfalfa from nutrient solutions in the presence of Al^{+++} , Mn^{++} , and H^+ is shown in tables 5 and 6. Aluminum showed the greatest depressive effect on Ca absorption. Upon addition of 10 ppm. Al^{+++} , the uptake of calcium was reduced to one-tenth of that in the control. Probably, over a growing season, the concentration of any one of the ions may be high enough in many acid soils to decrease significantly the absorption of calcium by plants.

The results would explain why an application of gypsum to an acid soil often fails to increase the calcium content of the plants (3, 11) even though the Ca^{++} concentration in the soil solution is markedly increased. The concentration of Al^{+++} and Mn^{++} in the soil solution may be greatly increased when gypsum is applied to acid soils (3, 11). Thus the low calcium content usually observed in plants grown on acid soils may be due to the antagonistic effect of Al^{+++} , Mn^{++} , and H^+ on the absorption of calcium as well as to the restricted root growth rather than to the low calcium supply in the soil.

SUMMARY AND CONCLUSIONS

Greenhouse experiments were conducted to study the influence of soil acidity and its associated factors on the absorption of calcium by alfalfa. Radiocalcium was used to label the CaCO_3 applied to the soil and the calcium supplied in nutrient solutions.

When the surface layer (0-3 inches) of an acid Mardin silt loam (pH 4.8) was limed, as much as 80 per cent of the calcium in the plants was derived from the limed layer overlying the acid subsoil. The relatively great uptake of calcium from the limed surface layer was due not only to the increased calcium supply in the limed layer but also to the deleterious effect of the acid subsoil on root growth and calcium absorption. The plants failed to develop normal taproots in the acid subsoil when only the 0-3½-inch layer of soil was limed.

In another experiment the amount of exchangeable calcium in the surface layer (0-2 inches) and the subsoil (2-10 inches) was kept constant at two pH values, 4.8 and 6.5, by diluting the limed layer with sand. Approximately the same proportion of the calcium in the plants was taken up from the surface layer at both pH values when the subsoil was maintained at pH 6.5. On the other hand, the proportion of calcium in the plants derived from the subsoil at pH 6.5 was greater than that at pH 4.8 when the pH of the surface layer was kept at 6.5. When CaCO_3 was localized with the seed, 10 to 30 per cent of the calcium in the plants was found to be derived from the applied lime.

The rate of absorption of calcium by alfalfa was markedly reduced in presence of Al^{+++} and, to a lesser degree, Mn^{++} and H^+ in nutrient solution.

Thus the low calcium content usually observed in plants grown on acid soils may be due to the antagonistic effect of Al^{+++} , Mn^{++} , and H^+ on the absorption of Ca^{++} as well as to the restricted root growth rather than to the low calcium supply in the soil.

REFERENCES

- (1) ARNON, D. I., FRATZKE, W. E., AND JOHNSON, C. M. 1942 Hydrogen-ion concentration in relation to absorption of inorganic nutrients of higher plants. *Plant Physiol.* 17: 515-524.
- (2) BATES, G. H. 1934 Relation of leaf size to root structure in *Trifolium repens*. *Jour. Ecol.* 22: 270-278.
- (3) FRIED, M., AND PEECH, M. 1946 Comparative effects of lime and gypsum upon plants grown on acid soils. *Jour. Amer. Soc. Agron.* 38: 614-623.
- (4) HENRIQUES, F. C., ET AL. 1946 Radioactive studies—analytical procedure for measurement of long lived radioactive sulfur, S35, with a Lauritzen electroscope and comparison of electroscope with special Geiger counter. *Indus. and Engin. Chem., Analyt. Ed.* 18: 349-353.
- (5) HEWITT, E. J. 1945 Resolution of the factors in soil acidity. *Long Ashton Res. Sta Ann. Rpt.* 1945: 51-60.
- (6) KIRSANOV, A. T. 1938 Experiments on new aspects of the problem of liming. *Trans. Dokuchaev Soil Inst.* 18: 7-35. (In Russian, English summary.)
- (7) MACKENZIE, A. J., AND DEAN, L. A. 1948 Procedure for measurement of P31 and P32 in plant material. *Analyt. Chem.* 20: 559-560.
- (8) PEECH, M., AND ENGLISH, L. 1944 Rapid microchemical soil tests. *Soil Sci.* 57: 167-195.
- (9) PEECH, M. 1945 Determination of exchangeable cations and exchange capacity of soils. Rapid micromethods utilizing centrifuge and spectrophotometer. *Soil Sci.* 65: 35-55.
- (10) POHLMAN, G. G. 1946 Effect of liming different soil layers on yield of alfalfa and on root development and nodulation. *Soil Sci.* 62: 255-266.
- (11) SCHMEHL, W. R., PEECH, M., AND BRADFIELD, R. 1950 Causes of poor growth of plants on acid soils and beneficial effects of liming: I. *Soil Sci.* 70: 393-410.
- (12) TRENEL, M., AND FREY, H. J. 1932 Über den Einfluss von löslichem und unlöslichem Aluminium auf die Nährstoffaufnahme von Roggen im Sandboden ohne und bei Gegenwart von Kieselsäurehydrat. *Chem. Ztg.* 56: 834.
- (13) WALLIHAN, E. F. 1948 Influence of aluminum on the phosphorus nutrition of plants. *Amer. Jour. Bot.* 35: 106-112.
- (14) WATENPAUGH, H. N. 1936 Influence of the reaction of soil strata upon the root development of alfalfa. *Soil Sci.* 41: 449-467.



MOVEMENT AND EFFECT OF LIME AND GYPSUM IN SOIL

DAVID RIRIE, STEPHEN J. TOTH, AND FIRMAN E. BEAR

New Jersey Agricultural Experiment Station¹

Movement of lime in soil is affected by fineness of division, rate of application, and placement of the liming materials; soil type; cropping system; and amount of water passing through the soil. The subject has been investigated in the field and with various types of lysimeters, lime-requirement tests, pH measurements, chemical analyses of both soils and leachates, and plant response being used as measurement criteria (1, 2, 3, 6, 7, 16, 21, 23, 24, 28).

The effect of liming materials on the outgo of various ions has been studied by MacIntire and associates over a period of years (9, 10, 11, 12, 13). Their work demonstrated that lime moved most rapidly during the first year after its application; $\text{Ca}(\text{OH})_2$ moved more rapidly than finely divided CaCO_3 or $\text{CaCO}_3 \cdot \text{MgCO}_3$; much of the lime moving downward from the surface layer was retained by the subsoil; CaCO_3 leached from coarse sand faster than $\text{CaCO}_3 \cdot \text{MgCO}_3$; Mg was lost from the soil at a faster rate than Ca when $\text{CaCO}_3 \cdot \text{MgCO}_3$ was applied; and K solubility in the incorporation zone was decreased by liming.

The purpose of this study was to determine the rate of movement of six liming materials and of gypsum and their effect on the soil when they were incorporated into the surface layers of two New Jersey soils, in a lysimeter type of test. A second test, involving the use of three Ca^{45} -tagged liming materials, was also performed to obtain supplementary information on rate of movement.

MATERIALS AND METHODS

Norton silt loam and Sassafra sandy loam were chosen for the test. Their field pH values, cation-exchange capacities, and exchangeable-cation contents were as follows:

SOIL	pH	ME. IN 100 GM. SOIL					
		H	Ca	Mg	Na	K	Cation-exchange capacity
Norton.....	4.5	15.03	2.65	2.04	0.13	0.16	21.01
Sassafra.....	4.0	2.20	0.33	0.11	0.12	0.12	2.88

Virgin A-horizon soil was collected, sieved through an 8-mesh screen, thoroughly mixed, and air-dried. The soil was then packed in pots, as shown in figure 1. The pots were mounted on tables, and collection flasks for leachates were placed under them. Each pot of Sassafra contained 22 pounds of soil, and each pot of Norton 20 pounds.

¹ Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, the State University of New Jersey, department of soils.

In the first test, commercial grades of CaCO_3 , CaO , $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{OH})_2 + \text{MgO}$, $\text{CaCO}_3 \cdot \text{MgCO}_3$, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and a reagent grade of MgO were used. The materials passed a 100-mesh but not a 140-mesh screen, except for the MgO , which passed through both.

The liming materials and the gypsum were added to the top 3 inches of soil in amounts equivalent to the H contained in the exchange complex of the entire $7\frac{1}{2}$ -inch soil column. Each treatment was replicated three times. Two controls of each soil were included in the test. The quantity of each liming material added was equivalent to more than twice the cation-exchange capacity of the 3-inch layer.

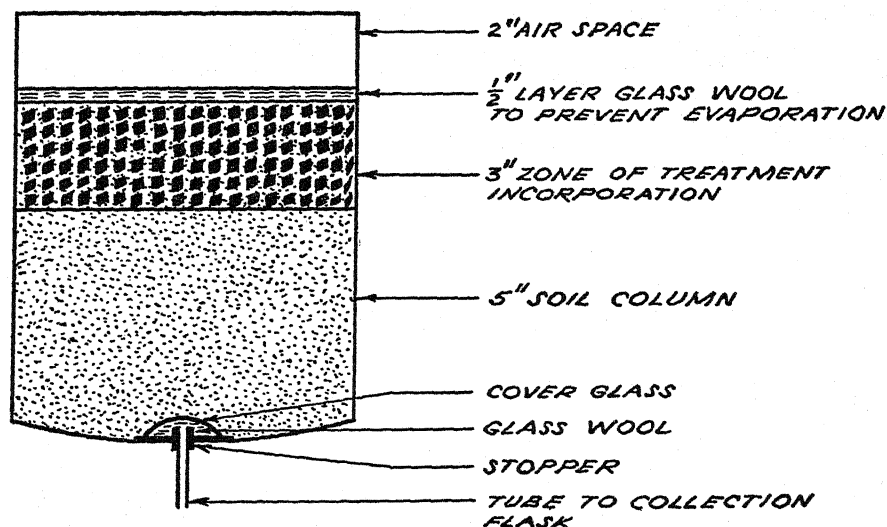


FIG. 1. CROSS SECTION OF INDIVIDUAL POT

The soil was covered with glass wool. Distilled water was added to each pot until it started to drain, after which increments of water, each equivalent to 2 inches, were applied. Leachates from the first eight increments were collected individually. The successive leachates were combined until a total of 44 inches had passed through each soil. This was assumed to be equivalent to the drainage that would occur on these soils over a 2-year period under field conditions. The percolates were tested at intervals for Ca, Mg, K, Na, and pH (25, 26).

At the conclusion of the leaching period, the soils were removed from the pots in three layers, designated as A, B, and C and having depths of 0 to 3, 3 to 5, and 5 to 7.5 inches, respectively. The average weight of a number of these layers was determined for use in later calculations. Exchangeable-cation status, free carbonate content, and pH value of each layer of soil were determined (26, 27).

Radioactive $\text{Ca}^{45}\text{CO}_3$, with a specific activity of 0.0947 mc. a gram, was used

in the second test.² CaCO_3 , CaO , and $\text{Ca}(\text{OH})_2$ were labeled with equivalent amounts of this material. Separate lots of the soils received the following amounts of tagged materials:

SOIL	$\text{Ca}^{45}\text{CO}_3$	Ca^{45}O	$\text{Ca}^{45}(\text{OH})_2$
	gm.	gm.	gm.
Sassafras.....	1.0	0.55	0.72
Norton.....	2.0	1.10	1.44

The tagged salts were thoroughly mixed with sufficient quantities of non-radioactive salts to be equivalent to the H contained in the exchange complex of the entire soil column. The salts were mixed with the top 3 inches of soil. Distilled H_2O , equivalent to the estimated drainage from 3 years' rainfall for New Jersey, or 66 inches, was applied to the soil in each pot. The leachates were periodically concentrated and analyzed.

Relative Ca^{45} activities of the leachates and extracts of the soil were estimated by the technique of Reid (19). Total Ca was first determined, and aliquots of the digest were then taken to yield 45 mgm. $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The Ca was precipitated in this form, collected on filter-paper discs, washed with 95 per cent ethyl alcohol, and mounted in a brass ring assembly. The activities of the precipitates were determined by means of a G. M. tube of window thickness of 1.89 mgm./cm.² and a Tracerlab autoscaler. The activities are expressed as disintegrations a minute in each leachate increment, or disintegrations a minute in each layer of soil.

RESULTS

Losses of Ca, Mg, K, and Na in leachings

Increased outgo of Ca occurred from the Norton soil following the use of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and of each form of lime (table 1). Loss of Ca from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ treatment was almost eight times as great as that from any of the others. Rate of movement of the Ca of $\text{Ca}(\text{OH})_2$, CaO , and $\text{Ca}(\text{OH})_2 + \text{MgO}$ was more rapid than that of the carbonates. An increased loss of Ca, almost equal in magnitude to that when CaCO_3 was used, occurred with MgO . This indicates that Mg from MgO replaced exchange Ca, which was leached out.

Similar results were obtained with Sassafras soil, but the data indicated a movement of Ca of the liming materials through the soil column. A far greater Ca outgo occurred from the calcitic than from the magnesian or dolomitic forms. The order of loss of Ca from the calcitic liming materials was: $\text{Ca}(\text{OH})_2 > \text{CaO} > \text{CaCO}_3$. Loss of Ca was greater from $\text{Ca}(\text{OH})_2 + \text{MgO}$ than from the $\text{CaCO}_3 \cdot \text{MgCO}_3$ treatment. The MgO applications seemed to conserve Ca.

All liming materials and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ caused Mg losses from the Norton soil. Losses following the use of $\text{Ca}(\text{OH})_2 + \text{MgO}$ were slightly greater than those

² The $\text{Ca}^{45}\text{CO}_3$ used in this investigation was supplied by the Oak Ridge Laboratories on authorization from the Isotopes Division, U. S. Atomic Energy Commission.

TABLE 1
Successive and total losses of Ca, Mg, K, and Na in leachates from Norton and Sassafras soils
Calculated in pounds an acre

TREATMENT	Ca				Mg				K				Na			
	1-5	6-10	11-18	Total	1-5	6-10	11-18	Total	1-5	6-10	11-18	Total	1-5	6-10	11-18	Total
<i>Norton silt loam</i>																
CaO.....	48	56	36	10	8	12	15	1	10	9	6	1	24	9	5	2
CaCO ₃	49	48	31	9	8	9	13	2	8	9	7	0	24	13	10	3
Ca(OH) ₂	49	62	34	8	9	13	14	2	8	12	5	2	27	10	7	2
CaCO ₃ ·MgCO ₃	51	48	34	8	10	10	13	2	9	9	6	2	23	10	9	2
Ca(OH) ₂ + MgO.....	50	51	38	12	7	12	22	2	8	10	5	2	25	8	6	1
CaSO ₄ ·2H ₂ O.....	391	307	369	133	61	51	70	6	14	22	7	2	45	20	4	0
MgO.....	46	47	34	9	7	10	15	1	9	9	6	2	26	8	7	2
Check.....	42	29	25	6	7	7	9	2	7	8	4	2	21	11	6	3
<i>Sassafras sandy loam</i>																
CaO.....	49	39	21	7	3	1	1	0	31	8	3	1	43	11	10	4
CaCO ₃	42	31	23	4	3	1	1	0	30	9	3	1	43	6	11	4
Ca(OH) ₂	58	34	29	5	2	2	1	0	28	8	3	0	39	11	10	3
CaCO ₃ ·MgCO ₃	28	17	13	3	5	6	3	1	15	29	8	2	42	9	12	3
Ca(OH) ₂ + MgO.....	46	18	12	3	7	5	6	0	17	27	3	0	37	3	1	6
CaSO ₄ ·2H ₂ O.....	444	153	75	14	686	4	0	0	4	42	9	0	56	2	2	1
MgO.....	23	4	4	1	32	20	12	8	31	7	4	0	42	35	4	5
Check.....	22	11	8	1	42	3	1	0	27	12	9	0	48	4	3	0

following the use of $\text{CaCO}_3 \cdot \text{MgCO}_3$. The Norton soil had a relatively high content of exchangeable Mg, which explains the heavy loss on treatment with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Other workers have reported variable results (8, 14, 22). Evidently the effects are governed by the nature of the soil. Considerably more Mg was lost from the Sassafras soil when it was treated with the Mg forms of lime, notably following the use of MgO.

Gypsum greatly increased the quantity of K released from both soils, especially from the Norton soil. Liming slightly increased K losses from the Norton and decreased them from the Sassafras soil. This difference in behavior is not surprising. Peech and Bradfield (15) have written:

A critical review of the literature reveals that the apparent confusion concerning the effect of lime and magnesia on the soil K and on the absorption of K by plants has arisen largely because of failure to evaluate properly, the experimental conditions under which the results were obtained and to distinguish the Ca-K interactions in the soil from those in the plant. The addition of lime to soils containing neutral salts (of strong acids) may have no effect, may decrease, or may increase the concentration of K in the soil solution, depending upon the initial degree of base saturation of the soil. In the absence of neutral salts, the addition of lime will invariably liberate the absorbed K even when an insufficient amount is added to neutralize all of the exchangeable H.

Early in the test, K was liberated in greater amounts from the limed Sassafras soil than from the control. Some of this released K may have been used by microorganisms (5).

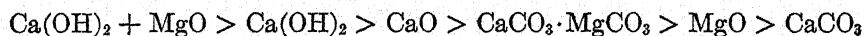
In contrast to its effects on K losses, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ repressed the outgo of Na from both soils. CaCO_3 increased the loss of Na from the Norton soil, whereas all other forms of lime had little or no effect. A greater loss of Na was noted when the soil was treated with $\text{CaCO}_3 \cdot \text{MgCO}_3$ than with $\text{Ca}(\text{OH})_2 + \text{MgO}$ or MgO. Na losses from the Sassafras soil were increased by all forms of calcitic lime and by $\text{CaCO}_3 \cdot \text{MgCO}_3$. MgO had little effect on Na outgo.

Losses of Ca from the Norton were highest in the first 10 and those from the Sassafras in the first 5 leachings. Losses of K and Na were highest during the first 10 leachings from both soils, but were more pronounced on the Sassafras. Losses of K and Na from the Norton did not decrease so rapidly with time as did those from the Sassafras soil.

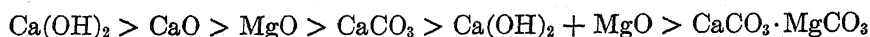
Maximum loss of Mg from the Norton occurred between the 6th and 18th leachings. Mg outgo from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ treatment was highest in the first 5 leachings, but a significant decrease was not observed until the 18th leachate. Mg outgo from the Sassafras decreased rapidly after the first 5 leachings from all except the magnesian forms of lime.

MacIntire (9) reported that most of the Ca lost from a soil occurs during the first year after liming. Jacobsen and associates (4) found that 90 per cent of the Ca, K, Na, and Mg was leached from the soil during the first 6 months after application. Except for Mg, these reports agree with our results.

When the movement of various liming materials through these soils is judged on the basis of the total Ca + Mg content of the leachates (table 2), the order of relative movement in the Norton soil is:



The order for the Sassafras sandy loam is:



Movement of liming materials within soils

Knowledge of the quantity and form in which the liming materials existed at the end of the test in the three layers of the two soils previously mentioned

TABLE 2
Losses of Ca and Mg in leachings from Norton and Sassafras soils

TREATMENT	NORTON SILT LOAM			SASSAFRAS SANDY LOAM		
	Ca	Mg	Total	Ca	Mg	Total
	me.	me.	me.	me.	me.	me.
CaO.....	34.5	13.1	47.6	29.5	2.5	32.0
CaCO ₃	30.5	11.7	42.2	25.0	2.3	27.3
Ca(OH) ₂	35.0	14.3	49.3	31.5	2.5	34.0
CaCO ₃ ·MgCO ₃	31.0	13.1	44.1	15.5	6.4	21.9
Ca(OH) ₂ + MgO.....	34.5	15.6	50.1	19.8	7.4	27.2
MgO.....	30.5	12.3	42.8	8.0	23.8	31.8
Check.....	23.0	9.9	32.9	11.0	2.5	13.5

TABLE 3
Effect of various liming materials and gypsum on the pH values of three layers of Norton and Sassafras soils

TREATMENT	NORTON SILT LOAM			SASSAFRAS SANDY LOAM		
	Layer A	Layer B	Layer C	Layer A	Layer B	Layer C
CaCO ₃	7.0	4.6	4.5	6.2	4.5	4.2
CaO.....	6.6	4.6	4.5	6.2	4.6	4.2
Ca(OH) ₂	7.6	4.8	4.5	6.3	4.5	4.2
CaCO ₃ ·MgCO ₃	6.8	4.6	4.5	6.1	4.5	4.2
Ca(OH) ₂ + MgO.....	7.7	4.7	4.5	6.0	4.4	4.2
CaSO ₄ ·2H ₂ O.....	4.4	4.4	4.4	4.3	4.3	4.2
MgO.....	7.9	4.9	4.6	6.6	4.9	4.3
Check.....	4.5	4.5	4.4	4.0	4.0	4.0
Original soil.....	4.5			4.0		

is important in evaluating their rates of movement. Changes in soil pH induced by incorporation of liming materials and CaSO₄·2H₂O are also of value in this connection (table 3). With the Sassafras soil, MgO applications produced a greater rise in pH values than any other liming material, at all depths. The other forms of lime produced very similar pH changes, layer by layer of soil. The rise in pH values approximated 2.2, 0.5, and 0.2 units for the top, middle, and lower layers, respectively. CaSO₄·2H₂O treatments produced a slight pH rise, which was about the same at all depths.

Greater differences in pH values were observed in the top layer of the Norton

TABLE 4
Ca and Mg present in carbonate and exchangeable forms in Norton and Sassafras soils

LAYER TREATMENT	Ca						PER CENT SATU- RATION WITH EX- CHANGEABLE Ca						Mg						PER CENT SATU- RATION WITH EX- CHANGEABLE Mg					
	Carbonate			Exchangeable			A			B			C			A						B		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C						
<i>Norton silt loam</i>																								
CaCO ₃	12.85	0.25	—	17.58	1.11	1.51	gm.	110	13	13	gm.	0.61	0.01	—	gm.	0.42	0.62	0.62	5	11	10			
CaO.....	10.83	0.23	—	20.44	1.35	1.51	gm.	127	15	13	gm.	0.64	0.01	—	gm.	0.88	0.56	0.68	10	10	12			
Ca(OH) ₂	8.68	0.19	—	20.68	2.08	1.53	gm.	128	22	13	gm.	0.39	0.01	—	gm.	1.46	0.33	0.35	16	6	6			
CaCO ₃ ·MgCO ₃	6.47	—	—	10.30	1.24	1.22	gm.	64	12	10	gm.	3.52	—	—	gm.	2.44	0.73	0.64	27	12	10			
Ca(OH) ₂ + MgO.....	1.12	—	—	13.53	1.76	1.42	gm.	88	17	12	gm.	0.62	—	—	gm.	4.26	1.00	0.64	48	17	10			
CaSO ₄ ·2H ₂ O.....	—	—	—	21.00	2.94	3.30	gm.	128	31	27	gm.	—	—	—	gm.	0.09	0.21	0.35	1	3	6			
MgO.....	—	—	—	2.14	1.42	1.58	gm.	13	14	14	gm.	—	—	—	gm.	15.44	0.72	0.66	173	12	10			
Check.....	—	—	—	2.33	1.53	1.44	gm.	15	15	12	gm.	—	—	—	gm.	0.87	0.57	0.67	10	10	10			
<i>Sassafras sandy loam</i>																								
CaCO ₃	0.42	—	—	3.46	0.30	0.09	gm.	142	20	6	gm.	0.02	—	—	gm.	0.02	0.01	0.01	1	1	1			
CaO.....	0.39	—	—	3.03	0.26	0.12	gm.	125	17	7	gm.	0.02	—	—	gm.	0.08	0.01	0.01	5	1	1			
Ca(OH) ₂	0.40	0.03	—	3.15	0.23	0.12	gm.	130	15	7	gm.	0.02	—	—	gm.	0.10	0.01	0.01	7	1	1			
CaCO ₃ ·MgCO ₃	0.88	—	—	1.48	0.26	0.10	gm.	61	17	6	gm.	0.47	—	—	gm.	0.11	0.005	0.005	7	—	—			
Ca(OH) ₂ + MgO.....	0.20	0.04	—	1.91	0.07	0.12	gm.	78	5	7	gm.	0.11	0.01	—	gm.	0.19	0.005	0.005	13	—	—			
CaSO ₄ ·2H ₂ O.....	—	—	—	0.51	0.63	0.38	gm.	20	42	24	gm.	—	—	—	gm.	0.01	0.01	0.01	1	1	1			
MgO.....	—	—	—	0.19	0.12	0.16	gm.	8	8	9	gm.	0.07	0.03	—	gm.	1.57	0.07	0.01	106	8	1			
Check.....	—	—	—	0.17	0.12	0.14	gm.	7	8	8	gm.	—	—	—	gm.	0.02	0.01	0.005	1	1	1			

than in that of the Sassafras soil. MgO again produced the greatest increases in pH values. With the calcitic forms the order of pH increases was: hydroxide > carbonate > oxide. All of the liming materials slightly increased the pH values of the B layer, but no effects were observed in the C. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ applications did not affect the pH value in any of the soil depths.

Free carbonates were not present in the C layer of either soil, and only small amounts were found in the B (table 4). In the Norton, the B layer contained carbonates only when calcitic materials were applied. Small amounts of carbonates were found in the B layer of Sassafras when $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{OH})_2 + \text{MgO}$, or MgO was applied to it. MgO had only a slight tendency to carbonate in the Sassafras soil. CaO and $\text{Ca}(\text{OH})_2$ did not revert completely to carbonate.

There was more than enough Ca + Mg in the exchange form to saturate the exchange complex of the A layer of the Norton soil, except where $\text{CaCO}_3 \cdot \text{MgCO}_3$ had been used. With this material the quantity of exchange Ca and Mg present was enough for only a 91 per cent saturation of the exchange complex. The exchange-Ca content of the B layer of Norton was nearly doubled by $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ applications. $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2 + \text{MgO}$ were the only liming materials to produce appreciable increases in exchange Ca, and CaCO_3 , $\text{CaCO}_3 \cdot \text{MgCO}_3$, and MgO decreased it. All forms of lime, except $\text{CaCO}_3 \cdot \text{MgCO}_3$ and $\text{Ca}(\text{OH})_2 + \text{MgO}$, increased the exchange Ca of the C layer, but the increases were small. The exchange-Ca content of this layer was more than doubled by the use of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ decreased the exchange-Mg content of all soil layers of Norton, indicating replacement of the Mg by Ca. $\text{Ca}(\text{OH})_2$ was the only liming material to decrease the exchange Mg content of the lower layers. There was evidence of downward movement of Mg into the B layer when magnesian liming materials were applied, but the C layer was virtually unaffected.

Except for the $\text{CaCO}_3 \cdot \text{MgCO}_3$ treatment on the Norton and the $\text{CaCO}_3 \cdot \text{MgCO}_3$, $\text{Ca}(\text{OH})_2 + \text{MgO}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ treatments on the Sassafras, the exchange complex of the A layer of both soils contained more exchange Ca + Mg than was required for saturation. Two explanations can be advanced. First, the Williams method employed in this study does not completely differentiate between carbonate and exchangeable forms of Ca and Mg. Secondly, the cation-exchange capacity of soils is increased by the use of liming materials, as observed by Rost and Zetterberg (20).

The exchange-Ca content of the B layer of Sassafras was unaffected by surface applications of MgO and slightly decreased by the use of $\text{Ca}(\text{OH})_2 + \text{MgO}$. All other forms of lime and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ increased the amount of exchange Ca in this layer. The exchange-Ca content of the C layer was virtually unaffected by any form of lime, but the use of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, increased it.

All liming materials and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ contained some Mg, and most of this remained in the A layer in the Sassafras soil. The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ applications decreased the amount of exchange Mg in this layer. MgO applications increased the exchange-Mg content of the B layer. None of the forms of lime had any marked effect on the amount of exchange Mg in the C layer.

To compare the movement of liming materials in the two soils, the total contents of exchange and carbonate forms of Ca and Mg in the three layers of each soil are presented on the equivalent basis (table 5). If the total exchangeable Ca + Mg content of the B depth of the Norton is used as a criterion for comparison, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and the hydroxide form of lime moved the fastest. With the exception of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the changes in the C layer were small.

The total exchangeable Ca + Mg of the B and C layers of Sassafras show that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ moves faster than any of the liming materials in this soil. Movement into the B layer of all liming materials except $\text{Ca}(\text{OH})_2 \cdot \text{MgO}$ was observed. CaCO_3 apparently accumulated in the B depth in greater amounts than the other forms. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ moved into the C layer, but the liming materials did not.

TABLE 5

Sum of exchangeable and carbonate forms of Ca and Mg in three layers of Norton and Sassafras soils at end of test

LAYER TREATMENT	Ca + Mg, NORTON SILT LOAM			Ca + Mg, SASSAFRAS SANDY LOAM		
	A	B	C	A	B	C
	me.	me.	me.	me.	me.	me.
CaCO_3	1605	120	125	197	16	6
CaO	1695	125	130	180	14	7
$\text{Ca}(\text{OH})_2$	1620	145	105	188	14	7
$\text{CaCO}_3 \cdot \text{MgCO}_3$	1330	120	115	166	13	5
$\text{Ca}(\text{OH})_2 + \text{MgO}$	1080	170	125	131	7	6
MgO	1380	130	135	145	14	9
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1060	170	195	27	33	20
Check.....	190	120	125	11	7	8

The exchangeable Ca + Mg of the A layers of both soils was higher when treated with calcitic than with magnesian materials. This may be explained by Mg-fixation, the possibility of which in New Jersey soils has previously been suggested (17, 18). Calcitic materials might possibly have neutralizing periods of greater duration than those resulting from the use of high-Mg materials on these soils.

Effect of lime and gypsum on exchange K and Na

The exchangeable K content of the A layer of Norton was increased by an MgO and decreased by a $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ application. All other applications had but a slight effect (table 6). K was released or conserved in the A layer of Sassafras by use of all liming materials and decreased by use of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The lower layers of both soils were affected to a lesser degree by the treatments, indicating that lime effects on exchange K are largely confined to the zone of incorporation.

Liming materials conserved exchange Na in the top 3 inches of Norton soil, but the two lower layers were almost depleted of the element when high-Ca

liming materials were applied. With high-Mg materials, this did not occur. Except for the MgO and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ treatments, almost all of the exchange Na in the Sassafras soil was lost by leaching.

TABLE 6

Exchange K and Na contents of three layers of the Norton and Sassafras soils at end of test

LAYER TREATMENT	NORTON SILT LOAM						SASSAFRAS SANDY LOAM					
	K			Na			K			Na		
	A	B	C	A	B	C	A	B	C	A	B	C
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
CaCO_3	0.21	0.14	0.15	0.07	0.005	0.005	0.14	0.06	0.06	0.005	0.0025	0.01
CaO	0.19	0.14	0.19	0.06	0.005	0.005	0.13	0.05	0.06	0.005	0.005	0.01
$\text{Ca}(\text{OH})_2$	0.19	0.13	0.18	0.06	0.005	0.005	0.13	0.06	0.07	0.005	0.01	0.01
$\text{CaCO}_3 \cdot \text{MgCO}_3$	0.23	0.14	0.19	0.02	0.02	0.01	0.14	0.04	0.06	0.005	0.005	0.01
$\text{Ca}(\text{OH})_2 + \text{MgO}$	0.17	0.11	0.20	0.04	0.02	0.01	0.14	0.06	0.04	0.005	0.01	0.01
MgO	0.35	0.16	0.20	0.07	0.01	0.03	0.14	0.05	0.05	0.03	0.02	0.02
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	0.12	0.10	0.12	0.06	0.05	0.03	0.07	0.03	0.05	0.02	0.02	0.01
Check.....	0.18	0.14	0.16	0.03	0.02	0.03	0.10	0.04	0.07	0.04	0.03	0.02

TABLE 7

Activities of leachates from Norton and Sassafras soils*

LEACHATE	NORTON SILT LOAM			SASSAFRAS SANDY LOAM		
	CaCO_3	CaO	$\text{Ca}(\text{OH})_2$	CaCO_3	CaO	$\text{Ca}(\text{OH})_2$
1	18	75	168	750	43,700	89,080
2	6	333	1,269	25,960	321,170	329,070
3	36	5,352	1,218	138,840	170,320	123,170
4	21	3,725	1,143	72,320	73,550	71,630
5	0	1,215	585	58,610	46,190	42,620
6	42	513	312	38,690	37,630	31,400
7	12	450	162	34,820	21,090	18,680
8	33	294	81	18,250	14,380	13,330
9	6	234	279	13,800	11,630	10,200
10	6	300	123	13,740	11,870	11,920
11	15	609	234	21,050	12,860	14,730
12	13	477	399	15,470	12,370	15,080

* Expressed as disintegrations a minute in each leachate increment.

Radioactive Ca^{45} studies

Assays of leachates for Ca^{45} showed that the maximum loss of liming materials occurred in the first three or four leachates (table 7). With the three forms used, only 0.002 per cent of $\text{Ca}^{45}\text{CO}_3$, 0.17 per cent of the Ca^{45}O , and 0.07 per cent of the $\text{Ca}^{45}(\text{OH})_2$ moved through the soil column. Little of the applied lime moved through the Norton, the leachate losses of Ca representing native Ca. Loss of lime from the Sassafras was greater than that from the Norton, but the

materials were leached in the same relative order. Losses of Ca45CO_3 , Ca45O , and Ca45(OH)_2 from the Sassafras soil were partly from the applied lime.

Data on exchangeable plus carbonate forms of Ca45 indicated that all liming materials migrated to some extent into the B and C layers (table 8). More Ca45 was found in the B layer from Ca45CO_3 than from the other two materials. Ca45CO_3 did not move into the C layer so readily as did the other materials. This agrees with the findings from the leachate analyses.

Approximately three times as much of the applied lime moved from the A into the B layer of the Sassafras as of the Norton soil. An even larger amount, relatively, moved into the C layer of the Sassafras, except for the Ca45CO_3 .

In Norton soil, the amount of lime that moved into the B layer was approximately 5.5 per cent and into the C layer about 0.3 per cent. Leachate losses amounted to less than 0.2 per cent. In Sassafras soil, the maximum amount of lime that moved into the B layer was 11 per cent and into the C layer 3 per cent.

TABLE 8

Distribution of Ca45 in three layers of Norton and Sassafras soils*

TREATMENT	NORTON SILT LOAM			SASSAFRAS SANDY LOAM		
	A	B	C	A	B	C
CaCO_3	6,378	365	13	2,185	363	1
CaO	7,287	175	18	2,458	231	66
Ca(OH)_2	6,470	165	15	2,407	277	95

* Expressed as total number, in thousands, of disintegrations a minute for each soil layer, Ca45 representing carbonate and exchange forms.

Leachate losses amounted to about 18 per cent. The movement of lime was considerably more rapid in the Sassafras than in the Norton soil.

SUMMARY AND CONCLUSIONS

A study was made of the movement of CaO , CaCO_3 , Ca(OH)_2 , $\text{CaCO}_3 \cdot \text{MgCO}_3$, $\text{Ca(OH)}_2 + \text{MgO}$, MgO , and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in Norton silt loam and Sassafras sandy loam, soils of widely different characteristics. The materials were incorporated into the top 3 inches of soil at rates equivalent to the H in the exchange complex of the entire $7\frac{1}{2}$ -inch soil column. Water was leached through the soils in amounts equivalent to the leaching from 2 years' rainfall for New Jersey. The percolates were analyzed at intervals for Ca, K, Na, and Mg. At the termination of the leaching, the soils were removed in layers, after which pH values, exchangeable Ca, Mg, K, and Na, and carbonate Ca and Mg were determined. Movement of CaO , CaCO_3 , and Ca(OH)_2 that had been tagged with Ca45 was also studied.

Ca and Mg losses from limed Norton silt loam consisted almost entirely of native soil constituents, whereas those from limed Sassafras sandy loam were derived almost entirely from the applied liming materials.

In both soils, the Ca of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was lost more rapidly than that from any of the liming materials.

Applications of liming materials caused an increased outgo of K from the Norton soil but tended to conserve K in the Sassafras soil. The K losses from both soils were increased by the use of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Application of CaCO_3 caused an increase in loss of Na from the Norton soil, but other forms of lime had little effect. On the Sassafras soil, use of calcitic forms of lime resulted in greater Na losses than use of magnesian forms. Loss of Na was repressed on both soils by use of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Use of any of the liming materials or of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ resulted in increased loss of Mg from the Norton soil. From the Sassafras soil, however, Mg was lost only when magnesian materials were applied.

The effects of applications of liming materials and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on the outgo of Ca and Mg were:

Norton silt loam: $\text{Ca}(\text{OH})_2 + \text{MgO} > \text{Ca}(\text{OH})_2 > \text{CaO} > \text{CaCO}_3 \cdot \text{MgCO}_3 > \text{MgO} > \text{CaCO}_3$

Sassafras sandy loam: $\text{Ca}(\text{OH})_2 > \text{CaO} > \text{MgO} > \text{CaCO}_3 > \text{Ca}(\text{OH})_2 + \text{MgO} > \text{CaCO}_3 \cdot \text{MgCO}_3$.

Liming materials moved downward considerably more slowly in the Norton than in the Sassafras soil. This was proved by pH measurements, by determinations of exchange Ca and Mg, and by use of radioactive Ca.

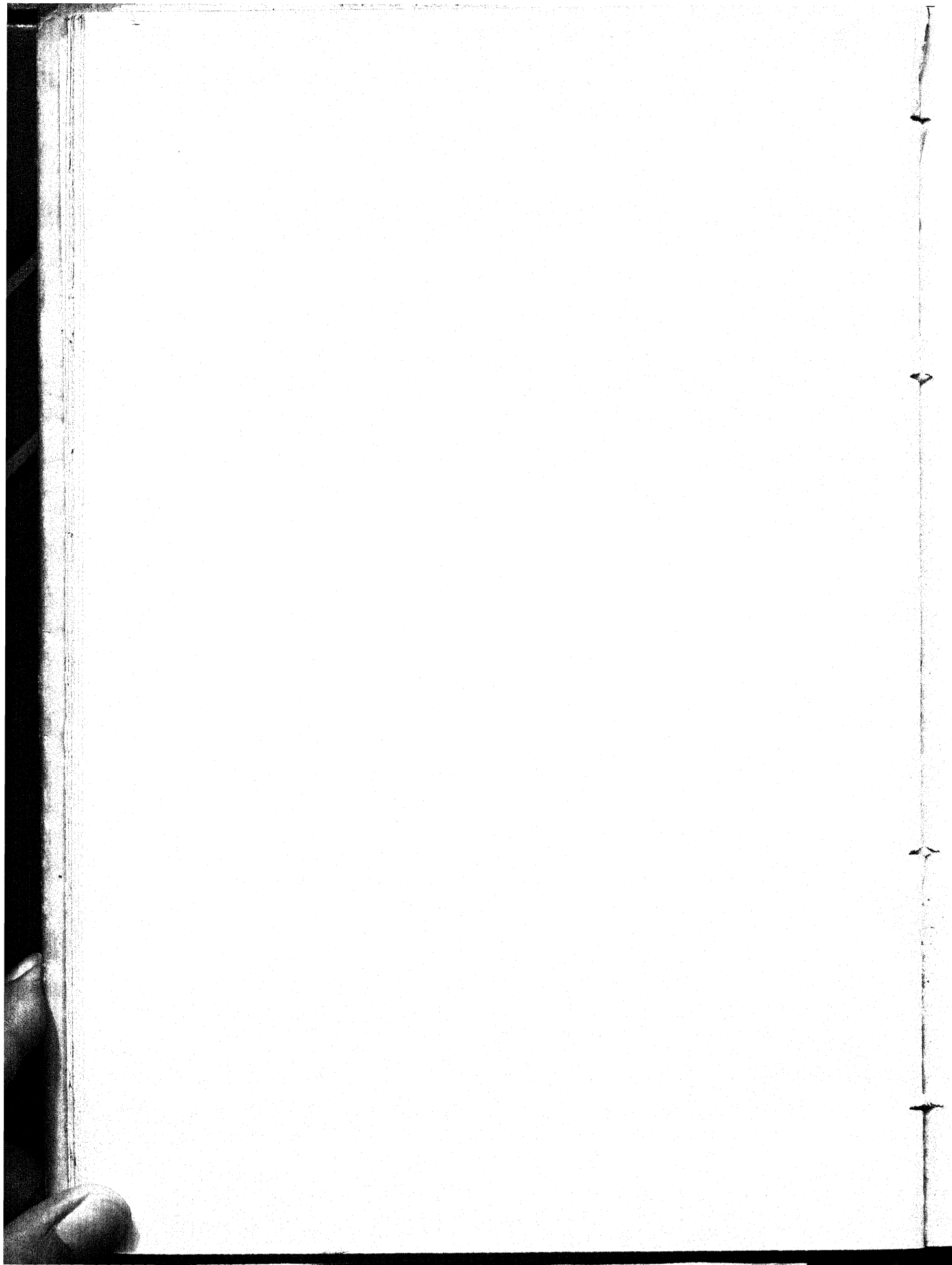
Considerable carbonation of burned and hydrated forms of lime occurred in the zone of incorporation.

On the Mg-fixing Norton soil, calcitic forms of lime appeared to have a neutralizing period of greater duration than the high-Mg forms of lime.

REFERENCES

- (1) BLAIR, A. W., AND PRINCE, A. L. 1934 Influence of lime on the reaction of subsoils. *Jour. Agr. Res.* 48: 469-473.
- (2) BROWN, G. A., AND MUNSEL, R. I. 1939 Soil acidity at various depths as influenced by time since application, placement, and amount of limestone. *Soil Sci. Soc. Amer. Proc.* (1938) 3: 217-221.
- (3) DORSEY, H. 1926 Some effects of limestone and hydrated lime on biochemical activities in acid soils. *Conn. Agr. Exp. Sta. Bul.* 141.
- (4) JACOBSEN, H. G. M., SWANSON, C. L. W., AND SMITH, E. 1948 Effect of various fertilizer cations and anions on soil reaction, leaching, nitrification of area, and related characteristics in an uncropped soil. *Soil Sci.* 65: 437-460.
- (5) JENNY, H., AND SHADE, E. R. 1934 The K-lime problem in soils. *Jour. Amer. Soc. Agron.* 26: 162-170.
- (6) LYON, T. L. 1921 Effect of liming on the composition of the drainage water of soils. *Jour. Amer. Soc. Agron.* 13: 124-130.
- (7) LYON, T. L., AND BIZZELL, J. A. 1921 Lysimeter experiments: II. N. Y. (Cornell) Agr. Exp. Sta. Mem. 41.
- (8) LYON, T. L., AND BUCKMAN, H. O. 1936 Lysimeter experiments: IV. N. Y. (Cornell) Agr. Exp. Sta. Mem. 194.
- (9) MACINTIRE, W. H. 1926 Influence of form, soil zone, and fineness of lime and magnesia incorporations upon the outgo of Ca and Mg. *Soil Sci.* 21: 377-391.
- (10) MACINTIRE, W. H., AND SHAW, W. M. 1926 Fixation of Ca-Mg from burnt lime, limestone, and dolomite incorporations in two soil zones. *Soil Sci.* 22: 109-121.

- (11) MACINTIRE, W. H. 1927 Outgo of Ca, Mg, nitrates, and sulfates from high calcic and magnesian limes incorporated in two soil zones. *Soil Sci.* 23: 175-197.
- (12) MACINTIRE, W. H., AND SHAW, W. M. 1930 Lime-magnesia ratios in dolomitic limestone as influencing solution and soil reactions. *Jour. Amer. Soc. Agron.* 22: 14-27.
- (13) MACINTIRE, W. H., ET AL. 1943 K retention from annual additions of Cl, SO₄, and NO₃, as influenced by limestone and by dolomite. *Soil Sci.* 55: 321-332.
- (14) MEHLICH, A., AND REED, J. F. 1946 Influence of degree of saturation, K level, and Ca additions on removal of Ca, Mg, and K. *Soil Sci. Soc. Amer. Proc.* (1945) 10: 87-93.
- (15) PEECH, M., AND BRADFIELD, R. 1943 Effect of lime and magnesia on the soil K and on the absorption of K by plants. *Soil Sci.* 55: 37-48.
- (16) POHLMAN, G. G. 1946 Effect of liming different soil layers on yield of alfalfa and on root development and nodulation. *Soil Sci.* 62: 255-266.
- (17) PRINCE, A. B. 1951 Magnesium economy in the Coastal Plain soils of New Jersey. *Soil Sci.* 71: 91-98.
- (18) PRINCE, A. L., AND TOTH, S. J. 1938 Effects of long-continued use of dolomitic limestone on certain chemical and colloidal properties of a Sassafras loam soil. *Soil Sci. Soc. Amer. Proc.* (1937) 2: 207-214.
- (19) REID, A. F. 1947 Preparation and Measurement of Isotopic Tracers. J. W. Edwards, Ann Arbor, Mich.
- (20) ROST, C. O., AND ZETTERBERG, J. M. 1932 Replaceable bases in the soils of south-eastern Minnesota and the effect of lime upon them. *Soil Sci.* 33: 249-277.
- (21) SELL, O. E., AND OLSON, L. C. 1947 Effect of surface applied phosphate and limestone on soil nutrients and pH of permanent pasture. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 233-245.
- (22) SHAW, W. M., MACINTIRE, W. H., AND HILL, H. H. 1949 Conservation of calcium and magnesium from inputs of burnt lime, limestone, dolomite, and dicalcium silicate, as influenced by rate and frequency of liming and zone of incorporation. *Va. Agr. Exp. Sta. Tech. Bul.* 112.
- (23) SMITH, A. M. 1933 Variation in the composition of the displaced soil solution. *2nd Internat. Cong. Soil Sci. Proc.* 2: 175-178.
- (24) STRASSER, G. A., MATHEWS, E. M., AND OBENSHAIN, S. S. 1945 Effect of certain fertilizers and lime treatments on some chemical properties of Cecil sandy loam. *Soil Sci. Soc. Amer. Proc.* (1944) 9: 159-163.
- (25) TOTH, S. J., ET AL. 1948 Rapid quantitative determination of eight mineral elements in plant tissue by a systematic procedure involving use of a flame photometer. *Soil Sci.* 66: 459-466.
- (26) TOTH, S. J., AND PRINCE, A. L. 1949 Estimation of cation-exchange capacity and exchangeable Ca, K, and Na contents of soils by flame photometer techniques. *Soil Sci.* 67: 439-445.
- (27) WILLIAMS, R. 1929 Determination of exchangeable bases in soils. *Jour. Agr. Sci.* 19: 589-599.
- (28) WILSON, B. J. 1918 Translocation of Ca in the soil. N. Y. (Cornell) Agr. Exp. Sta. Mem. 17.



EFFECT OF PARTICLE SIZE OF LIMESTONES ON SOIL REACTION, EXCHANGEABLE CATIONS, AND PLANT GROWTH

T. A. MEYER AND GARTH W. VOLK

Ohio Agricultural Experiment Station¹

The application of liming material to acid soils brings about many changes that generally result in better crops. The chemical composition of any liming material determines its total neutralizing power and hence its capacity to neutralize soil acidity. The degrees of fineness of the material determines the rate of solution in an acid soil. Thus, the degree of fineness largely determines the efficiency of a given liming material in correcting soil acidity.

Type of liming materials, degree of fineness, and rate of application together with the interrelationships between these factors are of increasing agronomic importance. In view of the variable nature of results obtained by many investigators, this study was undertaken to determine the relative effectiveness of various particle sizes of liming materials. This work considers in detail the influence of particle sizes, rate of application, and time after application¹ of liming materials upon reaction (pH) and exchangeable-cation changes in the soil and the effect of these changes on growth and chemical composition of alfalfa and soybeans.

REVIEW OF LITERATURE

Numerous investigations on the agricultural value of lime of different degrees of fineness have established the fact that the finer the material the quicker is its action in correcting soil acidity (2, 6, 8, 9, 10, 15, 18, 19). Salter (16) indicated that fineness is the important factor in choosing limestone. Walker and Brown (20) found that the amount of change in pH was a function of the degree of fineness of the limestone and the rate at which it was applied.

No apparent relationship was found between such physical properties as hardness, porosity, specific gravity, crystalline composition or chemical analysis and rate of solubility (12). Bear and Toth (4) estimated that when limestone particles passing a 150-mesh and retained on a 200-mesh screen are all dissolved, 87.5 per cent of the 65-100-mesh, 33.2 per cent of a 20-28-mesh, and 17.8 per cent of a 10-14-mesh material will have gone into solution. Pierre (14) calculated values for materials of different degrees of fineness and showed that the reaction time and the H-ion concentration of the soil are two factors affecting the neutralizing rate. White (21) calculated the relative values of limestone based on 100 for 100-mesh material, 69 for 60-mesh, 22 for 20-mesh, and 5 for 8-mesh. The investigations of Lyon (11) substantiated the conclusions of White. Coleman and Klemme (7) took as an index of comparative value the percentage of material passing a 12-mesh sieve. Albrecht (1) showed that small applications of 10-mesh limestone were relatively more effective than 100-mesh limestone as measured in corn yields.

The methods of evaluation were usually based on pH changes after treatment or on sieve analysis of material applied in comparison with crop yields. A method was developed by Bear and Allen (3), based on a complete sieve analysis, using an assumed value of α (the mean reduction in diameter of particles during the time of decomposition), and calculating efficiency factors therefrom. Salter and Schollenberger (17) estimated the efficiency of ground limestone when the size composition was represented by a straight line of best fit to the actual sieve analysis on a cumulative logarithmic plot. Later Schollenberger and

¹ Contribution from department of agronomy. The authors express their appreciation for many helpful suggestions by C. E. Evans.

Salter (19) described a chart for graphic evaluation of agricultural limestone which took into consideration such variables as time and chemical and size composition. These variables were carefully evaluated in experiments simulating practical field conditions.

MATERIALS AND METHODS

Two unlimed soils, Canfield silt loam and Crosby silt loam, were used in these studies. The lime requirement of the Canfield soil was 3 to 3.5 tons per acre, and that of the Crosby soil was 5 to 5.5 tons.

Two liming materials, hereafter designated as calcitic and dolomitic limestone, were compared in this study. The calcitic limestone had a total neutralizing power of 93 per cent and contained 51.3 per cent CaO and 0.5 per cent MgO. The dolomitic limestones had a neutralizing power of 103 per cent, with CaO and MgO contents of 29.84 per cent and 20.25 per cent, respectively. The follow-

TABLE 1

Particle size analysis of liming materials used in experimental tests

SIEVE NO.	TOTAL PERCENTAGE PASSING THROUGH U. S. STANDARD SIEVE					
	Screenings*		Meal*		Ground*	
	Dolomitic	Calcitic	Dolomitic	Calcitic	Dolomitic	Calcitic
4	100.0	100.0	100.0	100.0	100.0	100.0
8	92.2	91.2	94.0	92.5	96.0	94.7
20	42.0	41.2	58.6	64.7	80.0	86.0
30	32.0	33.6	49.4	54.6	75.5	76.0
40	25.0	28.3	42.4	47.3	69.5	68.0
50	20.0	23.0	36.8	40.3	62.5	61.0
60	18.2	20.7	33.8	37.0	58.0	58.0
80	16.0	16.9	30.8	31.8	52.0	52.0
100	14.4	14.4	28.4	28.4	48.0	48.0

* Agricultural limestone grades; these meet Ohio lime law specifications.

ing fractions, expressed in sieve numbers, were separated from each limestone: 4-8, 8-20, 20-30, 30-40, 40-50, 50-60, 60-80, 80-100, and < 100. Some of the fractions were mixed to prepare agricultural grades of screenings, meal, and ground limestone that would meet Ohio lime law specifications (table 1).

Each material was incorporated with the soils at rates of 1, 3, 5, and 10 tons per acre. All treatments were made in triplicate. The soils were periodically moistened with distilled water and sampled at intervals of $\frac{1}{2}$, $1\frac{1}{2}$, 3, 6, 9, 12, and 18 months after initial treatment. Before each sampling the soil was air-dried, removed from the pot, and thoroughly mixed. A 1:2 soil:water suspension stood 1 hour before pH was determined with a Beckman glass electrode.

After 18 months the Canfield soil was removed from the pots, and triplicated treatments were combined and thoroughly mixed. The composited sample was analyzed for exchangeable hydrogen, calcium, magnesium, manganese, and cation-exchange capacity by the methods as outlined by Peech *et al.* (13).

In the greenhouse studies, as in the pot reaction studies, Canfield silt loam (pH 5.0) was used. To correlate the two studies, the same fractions of calcitic

and dolomitic limestone were used. In addition, chemically pure MgO , CaO , and $Ca(OH)_2$ were included at rates based on equal neutralizing values. Each liming material was thoroughly incorporated with the soil at rates equivalent to 2, 3, 5, and 10 tons per acre. All treatments were triplicated, and each pot received phosphate and potash as soluble salts. The soil was then moistened and maintained at approximately field capacity for 2 weeks before planting. Alfalfa was used as the indicator crop. The average yield of five successive cuttings in triplicate was recorded as grams per pot, and the oven-dried plant material of the same treatments were analyzed for total calcium and magnesium.

After 10 months, during which five cuttings of alfalfa were made, the soil was removed from the pots, air-dried, thoroughly mixed, and samples were taken for pH determinations. Immediately thereafter, soybeans were planted without any additional fertilizer. All pots contained the same number of plants and were harvested when beans were forming. Soybean hay from the triplicated treatments were composited and analyzed for total calcium and magnesium. Following the harvest of soybean hay, the roots were removed, the soil was air-dried and triplicated treatments were composited and thoroughly mixed. Exchangeable hydrogen, calcium, magnesium, and manganese were determined on the soil samples by the methods of Peech *et al.* (13).

RESULTS AND DISCUSSION

Influence of particle size of liming materials on pH change in uncropped soils

The change in pH in Canfield silt loam depended more on size of particles and time after application than on type (calcitic or dolomitic) of limestone, as shown in figure 1. Obviously, all fractions caused an initial and immediate effect on the pH of the soil as shown by the $\frac{1}{2}$ -month readings for soils treated with 3 tons of liming material per acre. The smaller the particle size of the material, the greater the rise in soil pH. For example, at $\frac{1}{2}$ month the 4-8-mesh dolomitic material increased the pH by 0.13, whereas the material finer than 100-mesh caused a 1.60 pH increase over that of the soil receiving no limestone. Since the pH of a soil receiving limestone coarser than 20-mesh tended to decrease after $\frac{1}{2}$ month, it is thought that the initial rise was due to dust on the surfaces of the coarser particles. With particles finer than 20-mesh, however, gradual increases in pH with time after the initial reading indicated that these fractions are of some value in neutralizing soil acidity soon after application.

Progressively longer periods of time were required for the coarser particles to reach equilibrium with the soil acids. In general, the highest pH values occurred approximately 6 months after application for materials of 60-mesh or finer. For 50-60-mesh material, the highest pH was reached at about 12 months, whereas particles coarser than 50-mesh required at least 18 months to bring the soil to maximum pH values. Limestone particles coarser than 20-mesh had little value in correcting soil acidity, as was shown by the lack of appreciable change from the initial pH of 5.0 after 18 months' contact.

Calcitic limestone fractions generally produced higher pH values than the dolomitic limestone for corresponding particle size and rate during the first

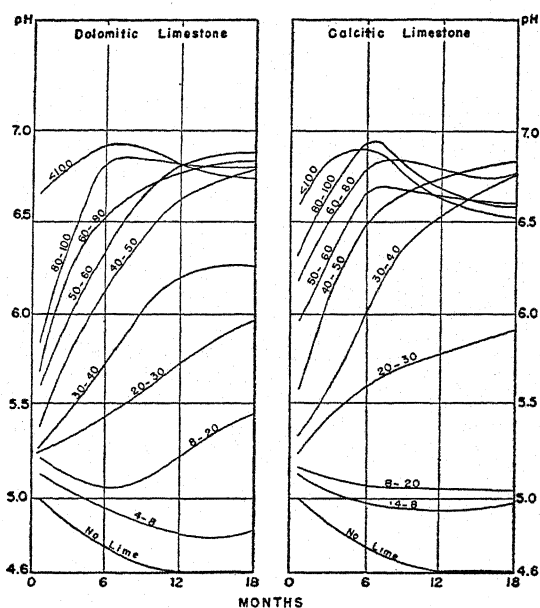


FIG. 1. INFLUENCE OF PARTICLE SIZE AND TIME AFTER APPLICATION OF LIMING MATERIALS ON pH OF UNCROPPED CANFIELD SILT LOAM

Limestone applied at a rate of 3 tons per acre. The soils were not cropped during the 18-month period. Figures on curves refer to U. S. standard mesh.

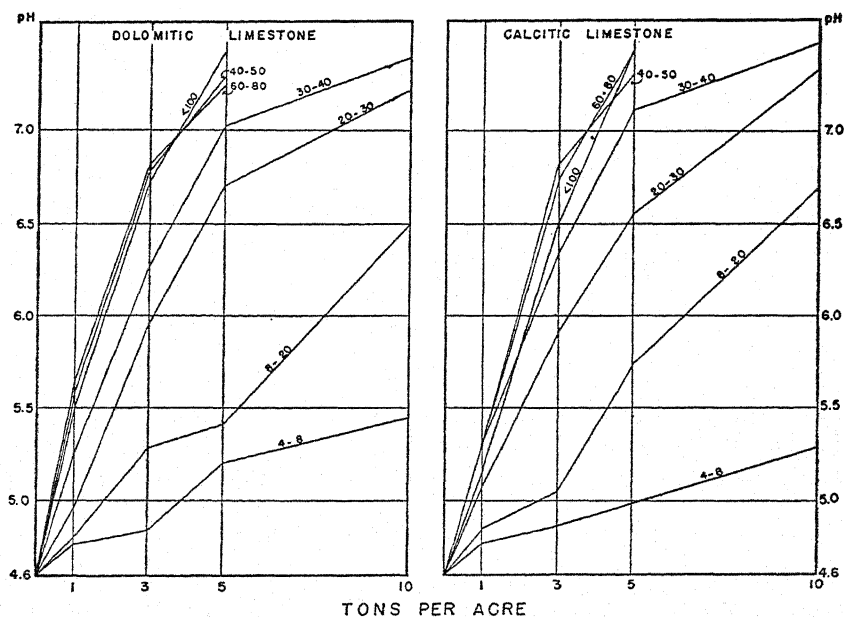


FIG. 2. INFLUENCE OF RATE AND PARTICLE SIZE OF LIMING MATERIALS ON pH OF UNCROPPED CANFIELD SILT LOAM

pH determinations were made at the end of 18 months. Figures on curves refer to U. S. standard mesh.

6 to 9 months after application. This tendency was also evident for the fractions coarser than 50-mesh 18 months after application. However, 9 months or longer after application, dolomitic material of 50-mesh or finer consistently gave higher pH values than did calcitic limestone of equivalent fineness at the 3-ton rate. These results were in agreement with those of other investigators that the initial rate of reaction of high-calcium limestone was slightly higher than that of dolomitic limestone. In this study, however, the rate of reaction differential between types of limestone appeared to be of minor practical significance.

When Crosby silt loam was treated with the same liming materials as the Canfield soil, similar relative trends were obtained. The finer sized particles were not so effective in correcting the acidity of Crosby soil because of the originally lower pH and higher base-exchange capacity of this soil. Furthermore, they took longer to reach equilibrium with this highly acid soil.

From these data it was apparent that the coarse 4-8-mesh material had little value in correcting soil acidity regardless of rate or time after application. The 20-30-mesh material applied at a 10-ton rate became effective after 18 months (fig. 2). All particle sizes finer than 40-mesh appeared to be approximately equal in their ability to neutralize soil acids. Apparently all liming material finer than 40 mesh was about 10 times as effective as 8-20-mesh material and about twice as effective as 20-30-mesh material.

Influence of liming material on exchangeable cations in uncropped soil

A gradual trend toward a higher cation-exchange capacity was noted heretofore when the soil was treated with increasing rates of limestone. Such a trend was also observed in this study. Moreover, the soil treated with calcitic limestone had a higher cation-exchange capacity than the soil similarly treated with dolomitic limestone.

Exchangeable hydrogen. As shown in table 2, exchangeable hydrogen in the Canfield soil decreased with increasing rates of both calcitic and dolomitic materials and with finer particle sizes used at a constant rate. The soil receiving 3 tons of the 4-8-mesh fraction contained 5.90 me. of exchangeable hydrogen per 100 gm., and that receiving material finer than 100-mesh, 2.40 me. These results indicate that the degree of fineness of the liming material influences the exchangeable hydrogen of the soil more than does the rate of application.

Exchangeable calcium. As calcitic limestone contains a higher percentage of calcium than does dolomitic limestone, it was expected that the Canfield soil treated with calcitic limestone would have higher exchangeable calcium values than the soil treated with dolomitic limestone. The results in table 3 show that as the rate of application of liming material was increased from 1 to 10 tons per acre, the exchangeable calcium increased. More striking, however, was the increase in exchangeable calcium with increasing degrees of fineness. The calcitic limestone applied at 3 tons per acre resulted in soils containing 4.1 me. of exchangeable calcium for the 4-8-mesh material and 8.6 me. for material finer than 100-mesh. When the rate of application of the coarse material (4-8-mesh) increased from 3 to 10 tons per acre the exchangeable calcium increased to only 6.1 me., or about 80 per cent over the untreated check.

TABLE 2

Influence of rate and particle size of liming materials on exchangeable hydrogen Canfield silt loam in uncropped pot culture studies after 18 months

PARTICLE SIZE, SCREEN	EXCHANGEABLE HYDROGEN, ME. PER 100 GM. SOIL*							
	Dolomitic limestone tons per acre				Calcitic limestone tons per acre			
	1	3	5	10	1	3	5	10
4-8		5.90	5.74	4.64		5.92	5.70	4.94
20-30	6.00	3.92	2.56	1.30		3.70	2.60	1.42
40-50	5.16	2.60	1.70		5.32	2.56	1.58	
60-80	5.04	2.40	1.66		5.22	2.44	1.40	
<100	3.86	2.40	1.28		4.04	2.40	1.42	
Screenings†	5.88	3.92	2.56		5.90	3.98	3.30	
Meal†	5.68	3.87	2.52		5.74	3.94	2.74	
Ground†	5.50	3.00	1.78		5.66	2.60	1.90	

* No lime = 6.60 me.

† Agricultural limestone grades.

TABLE 3

Influence of particle size and rate of limestone on exchangeable calcium and magnesium in uncropped soils after 18 months

TONS PER ACRE*	PARTICLE SIZE OF LIMING MATERIAL, U. S. STANDARD SCREENS					SCREENINGS†	MEAL†	GROUND†
	4-8	20-30	40-50	60-80	<100			
<i>Calcium, me./100 gm. soil‡</i>								
D 1		3.8	4.0	4.1		3.4	3.5	3.9
3	4.0	5.2	5.7	6.4	6.8	4.8	4.9	6.4
5	4.6	5.7	6.3	6.8		5.6	5.7	7.6
10	5.8	8.4						
C 1			4.5	4.7		3.9	4.4	4.6
3	4.1	6.8	7.6	8.1	8.6	6.0	6.5	7.4
5	4.8	8.4	10.3	10.3	10.4	7.4	7.5	10.1
10	6.1	11.2						
<i>Magnesium, me./100 gm. soil§</i>								
D 1		1.24	1.54	1.61		1.14	1.34	1.61
3	1.20	2.55	2.73	3.09	2.98	2.18	2.47	2.72
5	1.57	3.25	3.49	3.58	3.50	2.42	2.86	3.20
10	1.84	3.38						
C 1			0.87	0.76		0.88	0.89	0.87
3	1.00	0.88	0.85	0.81	0.80	0.84	0.78	0.74
5	0.87	0.90	0.62	0.51	0.46	0.83	0.64	0.66
10	0.82	0.64						

* D = dolomitic limestone; C = calcitic limestone.

† Agricultural limestone grades.

‡ No lime = 3.4 me.

§ No lime = 0.76 me.

Increases in exchangeable calcium of treated soils over untreated soils were used as an indication of the amount of calcium dissolved from the liming materials in 18 months. After 18 months only 13.4 per cent of the calcium contained in the 4-8-mesh calcitic material, when applied at 3 tons per acre, was dissolved. When the particle size was reduced to 40-50-mesh 72.5 per cent of the applied calcium was dissolved, and when reduced to finer than 100-mesh, 94.2 per cent.

Exchangeable magnesium. The data in table 3 show the amounts of exchangeable magnesium in soils incubated for 18 months after receiving different rates of liming materials of varying particle size. The soils treated with calcitic limestone showed a constant decrease in exchangeable magnesium with increasing rates and fineness. As more calcium dissolved, the amount of magnesium in an exchangeable form was apparently reduced. The dolomitic-treated soils showed

TABLE 4

Influence of rate and particle size of liming materials on exchangeable manganese of Canfield silt loam in uncropped pot culture studies after 18 months

PARTICLE SIZE, SCREEN	EXCHANGEABLE MANGANESE, ME. PER 100 GM. SOIL*							
	Dolomitic Limestone tons per acre				Calcitic Limestone tons per acre			
	1	3	5	10	1	3	5	10
4-8		.202	.152	.065		.260	.114	.073
20-30	.182	.048	.026	.036	.182	.056	.032	.040
40-50	.096	.030	.026		.107	.036	.025	
60-80	.087	.030	.023		.098	.028	.023	
<100		.024	.021			.030	.023	
Screenings†	.182	.061	.045		.182	.065	.051	
Meal†	.140	.048	.040		.114	.061	.045	
Ground†	.112	.041	.019		.112	.044	.020	

* No lime = 0.364 me.

† Agricultural limestone grades.

increases in exchangeable magnesium. When dolomitic limestone was applied at 3 tons per acre, for example, the 4-8-mesh material resulted in 1.2 me. of exchangeable magnesium per 100 gm. of soil as compared to 2.98 me. when finer than 100-mesh material was used.

The increase in exchangeable magnesium of the dolomitic-treated soils over the unlimed soil was used to calculate the percentage of applied magnesium dissolved. In general, there was a progressive reduction in the percentage of magnesium dissolved from any one fraction as the rate of application was increased. Evidently, with increasing degrees of fineness there was a corresponding increase in the percentage of applied magnesium which dissolved. Also evident was the greater percentage of calcium than magnesium dissolved from the dolomitic materials. This indicates again the greater dissolution of calcium.

Exchangeable manganese. It has been observed that soluble manganese in acid soils may be detrimental to plant growth and that liming acid soils inactivates toxic manganese. The influence of liming materials upon the content of exchange-

able manganese in soils is shown in table 4. Both calcitic and dolomitic treatment progressively reduced the exchangeable manganese when applied at increasing rates. The magnitude of reduction was greater, however, with increasing fineness of liming materials. In general, the dolomitic limestone reduced the exchangeable manganese to a greater degree than did the calcitic limestone, regardless of rate or fineness of material.

TABLE 5
Influence of rate and particle size of liming materials on yield of alfalfa grown in pot cultures on Canfield silt loam

PARTICLE SIZE, SCREEN	YIELD OF ALFALFA, GM. PER POT*							
	Dolomitic Limestone tons per acre				Calcitic Limestone tons per acre			
	2	3	5	10	2	3	5	10
4-8		4.9	5.3	5.6		5.3	6.0	6.8
8-20		5.0	6.1	6.5		5.6	7.1	8.1
20-30		6.4	6.3	8.2		7.5	9.3	9.3
30-40		6.5	7.6			8.0	8.5	
40-50		7.9	8.0			8.2	9.2	
50-60		7.9				8.8		
60-80		7.7				9.5		
80-100	8.2	8.7				9.5		
<100	7.8	8.3				9.5		
Screenings†		7.2	7.7			8.3	8.8	
Meal†		7.6	8.2			8.5	8.9	
Ground†	7.7	8.4	8.9		8.4	8.9	9.4	
MgO‡	8.2	8.1						
CaO‡					8.2	8.0		
Ca(OH) ₂ ‡					8.1	9.8		

* Average of five successive cuttings in triplicate. Yield with no lime = 4.6 gm.

† Agricultural limestone grades.

‡ Chemically pure material.

Influence of liming materials on crop growth and chemical content of forage

Alfalfa. The influence of rate and particle size of liming materials on the yield of alfalfa is shown in table 5. The yield increases with increasing fineness and rate. Soil treated with calcitic limestone yielded significantly more alfalfa than soil similarly treated with dolomitic limestone. A calcitic limestone application of 3 tons per acre caused a constant increase in yield as the degree of fineness was increased to 60-mesh, whereupon the yield remained approximately the same.

Altering the calcium and magnesium content in the soil causes a change in calcium and magnesium distribution in the plant. Bear and Prince (5) have suggested that, within limits, magnesium, calcium, and potassium may substitute for one another in the plant. The results shown in table 6 indicate that the percentage of calcium in forage increased and the percentage of magnesium decreased

with increasing fineness of calcitic materials. The total quantity of magnesium in the forage from any treatment remained approximately the same as the yield increased, whereas the total calcium increased with each increase in yield. With dolomitic limestone, total calcium and total magnesium increased as yield increased. These results indicate that calcium may be substituted for magnesium above the point where magnesium becomes limiting to plant growth.

TABLE 6

Influence of calcitic and dolomitic limestones, applied to Canfield silt loam at 3 tons per acre, on yield, Ca and Mg contents and Ca to Mg me. ratio of alfalfa grown in pot cultures

PARTICLE SIZE, SCREEN	DOLOMITIC LIMESTONE				CALCITIC LIMESTONE			
	Yield per pot*	Composition of forage			Yield per pot*	Composition of forage		
		Ca	Mg	Ca to Mg me. ratio		Ca	Mg	Ca to Mg me. ratio
No lime	gm. 4.6	% 1.52	% 0.48	5.2	gm. 4.6	% 1.52	% 0.48	5.2
4-8	4.9	1.52	0.47	5.3	5.3	1.54	0.44	5.7
8-20	5.0	1.52	0.48	5.2	5.6	1.79	0.43	6.7
20-30	6.4	1.58	0.48	5.4	7.5	1.90	0.43	7.1
30-40	6.5	1.60	0.48	5.4	8.0	1.98	0.39	8.2
40-50	7.9	1.56	0.49	5.2	8.2	1.92	0.38	8.1
50-60	7.9	1.52	0.49	5.0	8.8	1.87	0.35	8.8
60-80	7.7	1.50	0.51	4.8	9.5	1.78	0.31	9.2
80-100	8.7	1.49	0.52	4.7	9.5	2.00	0.32	10.1
<100	8.3	1.46	0.51	4.7	9.5	1.86	0.31	9.7
Screenings†	7.2	1.69	0.49	5.8	8.3	1.90	0.35	8.8
Meal‡	7.6	1.54	0.49	5.1	8.5	1.98	0.35	9.2
Ground‡	8.4	1.68	0.50	5.3	8.9	2.03	0.35	9.4
MgO‡	8.1	1.09	0.93	1.2				
CaO‡					8.0	1.93	0.30	10.2
Ca(OH) ₂ ‡					9.8	2.00	0.33	9.8

* Average of five successive cuttings in triplicate.

† Agricultural limestone grades.

‡ Chemically pure material applied on a CaCl₂-equivalent basis of 3 tons per acre.

It will be noted that the Ca to Mg me. ratio varies from 5.6 to 10.1 for the alfalfa grown on soils treated with calcitic limestone. The highest yields and ratios were induced by the finest materials. When dolomitic limestone was used, the ratio decreased from 5.28 to 4.70 as the yield and fineness increased. These data obviously show no direct correlation between yield and Ca to Mg me. ratio of the forage.

Soybeans. Soybeans are more tolerant of soil acidity than is alfalfa but are more demanding in their magnesium requirements. Table 7 shows that the yields of soybean hay were higher on soils treated with dolomitic limestone than

on those treated with calcitic limestone. Dolomitic material finer than 100-mesh increased yields by 63 per cent over no lime. The maximum yield, 13.3 gm. per pot, from calcitic limestone was obtained with the application of 60-80-mesh material; material finer than 100-mesh reduced this yield by 1.40 gm., or 10 per cent. This reduction in yield, which was accompanied by lower content of magnesium in plant tissue and lower exchangeable magnesium in the soil, might suggest a magnesium deficiency.

The percentage calcium in soybean hay was approximately constant, 1.19 to 1.29 per cent, regardless of yield or of treatment with dolomitic limestone (table 7). It increased substantially, from 1.30 to 1.83 per cent, with increased yield

TABLE 7

Influence of fineness of limestones, applied to Canfield silt loam at 3 tons per acre, on yield Ca and Mg contents, and Ca to Mg me. ratio of soybean hay

PARTICLE SIZE, SCREEN	DOLOMITIC LIMESTONE				CALCITIC LIMESTONE			
	Yield	Ca	Mg	Ca to Mg me. ratio	Yield	Ca	Mg	Ca to Mg me. ratio
	gm.	%	%		gm.	%	%	
4-8	8.9	1.19	0.48	4.1	7.8	1.30	0.49	4.0
20-30	11.9	1.25	0.61	3.3	10.8	1.61	0.50	5.3
40-50	12.1	1.29	0.71	3.0	12.2	1.66	0.49	5.6
60-80	14.1	1.27	0.78	2.7	13.3	1.76	0.48	6.1
<100	14.7	1.29	0.77	2.8	11.9	1.83	0.41	7.3
Screenings*	11.4	1.27	0.66	3.2	12.0	1.67	0.47	5.9
Meal*	12.1	1.24	0.68	3.1	12.3	1.63	0.48	0.7
Ground*	11.6	1.34	0.79	2.8	11.2	1.65	0.48	5.7
MgO†	9.7	0.67	1.19	0.9				
CaO†					12.0	1.78	0.44	6.4
Ca(OH) ₂ †					11.3	1.73	0.45	6.3

* Agricultural limestone grades.

† Used instead of limestone at 3 tons per acre equivalent.

and fineness and rate of calcitic limestone; the reverse was true for the percentage of magnesium. The percentage of magnesium was significantly higher in soybean hay than in alfalfa for both dolomitic and calcitic treatments. This accounts for the fact that the Ca to Mg me. ratio is lower for soybean hay than for alfalfa. Apparently the ratio can vary widely without affecting soybean yields.

Influence of liming material on chemical content of cropped soils

The effect of removing calcium and magnesium from the soil system by plant growth is indicated by a comparison of the pH values in figures 3 and 4 with those in figure 1. The soil reaction 12 months after application was significantly higher on uncropped soils than on similarly treated but cropped soils 10 months after application. After cropping, the pH values were generally higher in the soils treated with calcitic limestone than in the soils treated with dolomitic limestone.

Exchangeable hydrogen. It was previously shown in the uncropped pot culture

study that after 18 months the exchangeable hydrogen decreased with increasing rate of both calcitic and dolomitic limestone and with increasing fineness of particles. Although the greenhouse study was conducted for only 14 months prior to exchangeable-cation determinations the same trend occurred as in the uncropped pot culture study. Table 8 shows that the greatest reduction in exchangeable hydrogen occurred with the application of materials finer than 40-mesh. This indicates the greater effectiveness of these finer sized particles in the neutralization of soil acids under the influence of plant growth.

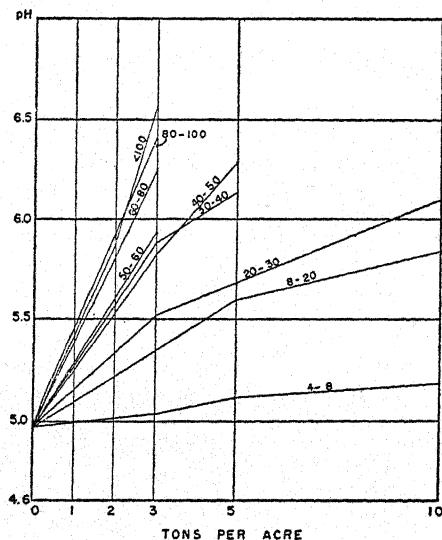


FIG. 3

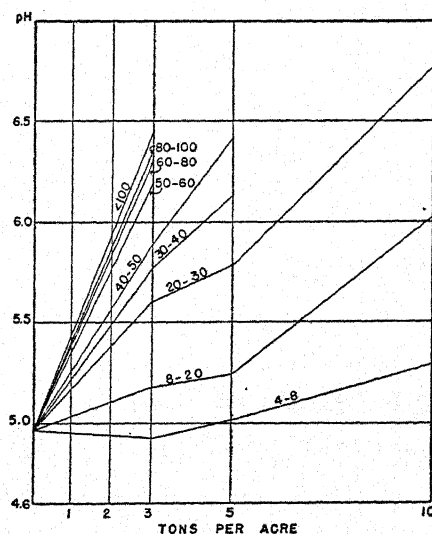


FIG. 4

FIG. 3. INFLUENCE OF RATE AND PARTICLE SIZE OF DOLOMITIC LIMESTONE ON pH OF CROPPED CANFIELD SILT LOAM

pH determinations were made at the end of 10 months; five crops of alfalfa were grown in this period.

FIG. 4. INFLUENCE OF RATE AND PARTICLE SIZE OF CALCITIC LIMESTONE ON pH OF CROPPED CANFIELD SILT LOAM

pH determinations were made at the end of 10 months; five crops of alfalfa were grown in this period.

Exchangeable calcium. The exchangeable calcium in Canfield silt loam, after 14 months' cropping, was higher when treated with calcitic limestone containing 51.29 per cent calcium than when treated with dolomitic limestone containing 29.84 per cent calcium. As shown in table 8, the calcitic limestone applied at 3 tons per acre caused an increase in exchangeable calcium from 2.57 me. for the 4-8-mesh to 6.78 me. for the material finer than 100-mesh, whereas the dolomitic limestone treatments of the same particle size caused an increase from 2.46 me. to 4.77 me. The chemically pure MgO treatment reduced the calcium content 0.36 me. below that of the no-lime treatment, whereas the $Ca(OH)_2$ and CaO increased the calcium content by 4.39 and 4.20 me.

The percentage calcium dissolved from added calcitic and dolomitic limestones was very low for the 4-8-mesh material, but 89 per cent was dissolved when

particles of 60-80-mesh were used. There was little difference in the effectiveness of limestone fractions finer than 60-mesh after 14 months' contact with the soil.

Exchangeable magnesium. Increasing fineness of calcitic limestone applied to Canfield soil at 3 tons per acre caused a gradual reduction in exchangeable magnesium. The results in table 8 indicate again that when the particle size of dolomitic stone was reduced, the amount of magnesium dissolved was correspondingly increased. Only 9 per cent of the magnesium in 4-8-mesh dissolved, whereas 90 per cent in the material finer than 100-mesh dissolved in 14 months.

Exchangeable manganese. The influence of liming materials and plant growth upon exchangeable manganese is also shown in table 8. As numerous other investigations also have shown, exchangeable manganese is reduced when liming

TABLE 8

Influence of fineness of limestones applied at 3 tons per acre, on exchangeable hydrogen, calcium, magnesium, and manganese in Canfield soil cropped to alfalfa and soybeans

PARTICLE SIZE, SCREEN	DOLOMITIC LIMESTONE				CALCITIC LIMESTONE			
	H	Ca	Mg	Mn	H	Ca	Mg	Mn
	me.*	me.	me.	me.	me.	me.	me.	me.
4-8	7.0	2.46	0.93	0.049	7.0	2.57	0.49	0.067
20-30	5.7	3.32	1.53	0.048	5.2	5.10	0.49	0.034
40-50	4.8	3.76	2.25	0.035	4.2	6.36	0.48	0.017
60-80	3.5	4.55	2.94	0.019	3.6	7.00	0.47	0.014
<100	3.2	4.77	3.14	0.015	3.2	6.78	0.43	0.013
Screenings†	5.5	3.42	1.55	0.035	5.1	3.54	0.46	0.025
Meal†	5.3	3.19	1.85	0.030	4.8	4.08	0.50	0.020
Ground†	4.2	4.41	2.50	0.018	4.0	6.27	0.51	0.015
No lime	7.3	2.48	0.56	0.091				

* Me. = per 100 gm. soil.

† Agricultural limestone grades.

materials are applied. This may partly explain the presence of manganese-deficiency symptoms in soybeans following heavy lime applications.

Relationship of calcium and magnesium in plant tissue to that in exchangeable form in soil

Equivalent quantities of calcium to magnesium in exchangeable form in the soil and in plant tissue were calculated as the Ca to Mg me. ratio (table 9). There was no difference in the ratio for the unlimed cropped and uncropped soil. An application of dolomitic materials to the uncropped soil greatly reduced this ratio. The ratio was relatively unaffected after the lowest value of 2.0 was obtained for the 20-30-mesh material. Dolomitic limestone applications to the cropped soil also resulted in a reduction of the ratio from that of the no-lime treatment, and as the particle size was reduced from 4-8-mesh to finer than 100-mesh, the ratio was reduced from 3.0 to 1.5.

Although the ratio values are appreciably higher for alfalfa than for soybeans in the no-lime treatment, they decreased for both crops with decreasing

particle size of dolomitic limestone. Increasing the degrees of fineness of calcitic materials resulted in a much higher ratio.

Bear and Prince (5) have suggested that the ratio for Ca to Mg in the ideal soil is 6.5. In this investigation, however, a Ca to Mg ratio of 15.0 in the soil produced the highest yield of alfalfa and 1.52 produced the highest yield for soybeans on the same soil but treated with limestones finer than 100-mesh.

TABLE 9

Ratio of calcium to magnesium in crops as related to that in exchangeable form in cropped and uncropped Canfield silt loam receiving calcitic and dolomitic limestone of various particle sizes

PARTICLE SIZE, SCREEN*	CALCIUM TO MAGNESIUM ME. RATIO			
	Exchangeable form in soil		In plant tissue	
	Uncropped†	Cropped‡	Alfalfa‡	Soybeans‡
No lime	4.4	4.4	5.2	4.07
<i>Dolomitic limestone</i>				
4-8	3.3	3.8	5.3	4.1
20-30	2.0	2.2	5.4	3.3
40-50	2.1	1.7	5.2	3.0
60-80	2.1	1.6	4.8	2.7
<100	2.3	1.5	4.7	2.8
<i>Calcitic limestone</i>				
4-8	4.1	5.2	5.7	4.3
20-30	7.7	10.5	7.1	5.3
40-50	9.0	13.1	8.1	5.6
60-80	10.0	15.0	9.2	6.1
<100	10.7	15.9	9.7	7.3

* Applied at rate of 3 tons per acre.

† Determinations made after 18 months for uncropped soils and 14 months for cropped soils.

‡ Average in five cuttings of alfalfa and in one crop of soybeans that followed the last cutting of alfalfa.

Average relative efficiency of limestone particle size fractions

The effects on crop yield and on certain soil changes were considered as a basis for evaluating the efficiency of limestone particle size fractions. Alfalfa was chosen as the crop because five successive cuttings in 12 months would be more significant than one crop of soybeans. Relative values were based on 0 for the no-lime treatment and 100 for the material passing a 100-mesh sieve when all fractions were applied at 3 tons per acre. The average relative efficiency of the various fractions is the mean of the relative values.

The results in table 10 show that the average relative efficiency of the calcitic materials is constantly higher than that of corresponding dolomitic materials. More important is the fact that the 4-8-mesh calcitic and dolomitic limestones

had negligible relative efficiencies of 5 and 8. A substantial increase in relative efficiency to 39 and 54 was obtained for the 20-30-mesh fraction. This material, however, was not fine enough to cause significant soil changes and increases in plant growth within a practical period. The data further indicate that the average relative efficiency value of 74 for the 40-50-mesh calcitic material was of practical significance. For comparable effectiveness, dolomitic limestones should be 60-80-mesh.

TABLE 10

Influence of lime fineness on alfalfa yield in pot cultures and on pH, exchangeable Y, Ca, and Mg in Canfield silt loam

PARTICLE SIZE, SCREEN	pH	YIELD OF AL- FALFA PER POT	EXCHANGEABLE IONS PER 100 GM. SOIL		AVER- AGE RELA- TIVE EFFI- CIENCY	pH	YIELD OF AL- FALFA PER POT	EXCHANGEABLE IONS PER 100 GM. SOIL			AVER- AGE RELA- TIVE EFFI- CIENCY
			Hydro- gen de- crease	Calcium increase				Hydro- gen de- crease	Cal- cium in- crease	Mag- nesium in- crease	
<i>Calcitic limestone*</i>						<i>Dolomitic limestone*</i>					
No lime <100	4.96	gm. 4.60	mc. 7.26	mc. 2.48		4.96	gm. 4.60	mc. 7.26	mc. 2.48	mc. 0.56	
	6.45	9.51	3.24	6.78		6.56	8.39	3.22	4.77	3.14	
<i>Relative values</i>						<i>Relative values</i>					
No lime	0	0	0	0	0	0	0	0	0	0	1
4-8	-3	16	7	2	5	5	10	6	8	10	8
20-30	44	60	51	61	54	35	49	38	37	37	39
40-50	62	72	76	90	74	53	89	61	56	65	65
60-80	91	99	90	103	96	80	82	92	90	96	84
<100	100	100	100	100	100	100	100	100	100	100	100
Screenings†	52	72	53	24	50	40	69	43	41	38	46
Meal†	62	77	61	37	59	44	81	50	31	50	51
Ground†	79	85	82	88	84	67	102	76	84	75	81

* Calcitic and dolomitic limestones applied at 3 tons per acre.

† Agricultural limestone grades.

A comparison of the calcitic and dolomitic agricultural limestone grades shows that the average efficiency of the screenings was approximately equal to that 20-30-mesh material. This was to be expected, since 68 per cent of the material in screenings is coarser than 30-mesh. With 50 per cent of the material coarser than 30-mesh, the grade classified as meal, the average efficiency was slightly higher than that of the 20-30-mesh. The efficiency of the ground grade of calcitic limestone was considerably higher than the minimum practical efficiency of the 40-50-mesh material. The efficiency of the ground grade of dolomitic limestone was appreciably higher than that of 40-50-mesh dolomitic limestone but equaled that of the same grade of calcitic limestone.

These data indicate that from the practical standpoint, if limestone is to be applied in amounts for optimum plant growth, a large portion should be ground

sufficiently fine to pass a 40-mesh sieve. Furthermore, there would seem to be little advantage in having the limestone ground as fine as 100-mesh if cost of additional grinding is taken into consideration. Of course, if maximum effects from the liming material are desired in less than a year after application, these finer materials are to be desired.

SUMMARY

An investigation using uncropped pot cultures was conducted in the laboratory to ascertain the effects of various sized particles of a calcitic and a dolomitic limestone upon soil reactions after various periods and upon exchangeable cations in the soil. In addition, a greenhouse experiment on the same soil was set up to determine the effects of various sized lime particles upon the yield and chemical composition of alfalfa and soybeans, and upon pH and exchangeable cation changes in the soil.

Results of the uncropped pot culture investigation indicated that liming particles coarser than 20-mesh had little or no value in correcting soil acidity. Liming materials varying in particle size from 20 to 60-mesh induced little initial soil reaction change, but after 18 months approached the effectiveness of finer sized particles. Particles finer than 100-mesh reacted soon after application but decreased in effectiveness after 18 months.

Calcitic limestone was slightly more effective than dolomitic limestone in correcting soil acidity after 6 to 9 months; however, the dolomitic form finer than 50-mesh induced higher pH values after 9 months. The results showed that agricultural limestones are dependent upon the percentage of material finer than 40-mesh for initial correction and maintenance of a favorable soil reaction. Agricultural ground limestone, of which 70 per cent was finer than 40-mesh, was found to be more efficacious than meal or screenings.

After 18 months' incubation, there was a consistent decrease of exchangeable hydrogen and increase of exchangeable calcium and magnesium in the soil with increasing degrees of fineness for dolomitic materials. Calcitic materials of an extremely low magnesium content exercised a repressive effect on the exchangeable magnesium. The percentage of applied calcium and magnesium dissolved and in an exchangeable form in the soil was largely a function of the degree of fineness of liming materials. Exchangeable manganese decreased with increasing fineness of both calcitic and dolomitic materials and was an inverse function of pH.

In the greenhouse studies, alfalfa yields were higher on the soils treated with treated with calcitic than with dolomitic limestone materials and increased with increasing rate and fineness of particles. Soybean yields were higher on the dolomitic-treated soils, and also increased with increasing degrees of fineness.

The percentage of calcium absorbed by alfalfa grown on calcitic-treated soils increased and the percentage of magnesium decreased with increasing particle fineness. The reverse was true on the dolomitic-treated soils. These same trends were observed for the percentages of calcium and magnesium in soybean hay.

The calculated average relative efficiency of the various particle sizes justifies the conclusion that 4-8-mesh material has little or no value as a liming material;

that 20-30-mesh material may become effective over extended periods; and in order that agricultural limestone grades be effective within a year after application, a large portion must be ground sufficiently fine to pass a 40-mesh sieve.

REFERENCES

- (1) ALBRECHT, W. A. 1946 Plant nutrition and the hydrogen ion: V. *Soil Sci.* 61: 265-271.
- (2) BAUER, F. C., AND SNIDER, H. J. 1926 Extreme fineness in limestone not necessary. *Ill. Agr. Exp. Sta. Ann. Rpt.* 1926: 16-17.
- (3) BEAR, F. E., AND ALLEN, L. 1932 Relation between fineness of limestone particles and their rates of solution. *Indus. and Engin. Chem.* 24: 998-1001.
- (4) BEAR, F. E., AND TOTH, S. J. 1942 The pH values and lime requirements of 20 New Jersey soils. *N. J. Agr. Exp. Sta. Cir.* 446.
- (5) BEAR, F. E., AND PRINCE, A. B. 1948 Magnesium needs of New Jersey soils. *N. J. Agr. Exp. Sta. Bul.* 739.
- (6) BROUGHTON, L. G., WILLIAMS, R. C., AND FAYEE, G. S. 1916 Tests on the availability of different grades of ground limestone. *Md. Agr. Exp. Sta. Bul.* 193.
- (7) COLEMAN, O. T., AND KLEMME, A. W. 1941 Liming Missouri soils. *Missouri Agr. Exp. Sta. Cir.* 218.
- (8) FREAR, W. 1921 Fineness of lime and limestone application as related to crop production. *Jour. Amer. Soc. Agron.* 13: 171-84.
- (9) HARTWELL, B. L., AND DAMON, S. C. 1919 A field comparison of hydrated lime with limestone of different degrees of fineness. *R. I. Agr. Exp. Sta. Bul.* 180.
- (10) KOPELOFF, N. 1917 Influence of fineness of division of pulverized limestone on crop yield as well as the chemical and bacteriological factors in soil fertility. *Soil Sci.* 4: 19-70.
- (11) LYON, T. L. 1931 Relative effectiveness of limestone particles of different sizes. *N. Y. (Cornell) Agr. Exp. Sta. Bul.* 531.
- (12) MORGAN, M. F., AND SALTER, R. M. 1923 Solubility of limestones as related to their physical properties. *Soil Sci.* 15: 293-305.
- (13) PEECH, M., et al. 1947 Methods of soil analysis for soil-fertility investigations. *U. S. Dept. Agr. Cir.* 757.
- (14) PIERRE, W. H. 1930 Neutralizing values and rate of reaction with acid soils of different grades and kinds of liming materials. *Soil Sci.* 29: 137-58.
- (15) ROST, C. O., AND FIEGER, E. A. 1927 Effects of different kinds and amounts of liming materials upon the hydrogen ion concentration of the soil. *Proc. and Papers First Internatl. Cong. Soil Sci.* 2: 45-65.
- (16) SALTER, R. M. 1929 Choosing the right liming material. *Ohio Agr. Exp. Sta. Spec. Circ.* 24.
- (17) SALTER, R. M., AND SCHOLLENBERGER, C. J. 1940 Criteria for the evaluation of agricultural ground limestone. *Symposium on Lime* 1939: 71-82. *Amer. Soc. Testing Materials*, Philadelphia.
- (18) SCHOLLENBERGER, C. J. 1921 Lime requirement and reaction of lime materials with soil. *Soil Sci.* 11: 261-276.
- (19) SCHOLLENBERGER, C. J., AND SALTER, R. M. 1943 A chart for evaluating agricultural limestone. *Jour. Amer. Soc. Agron.* 35: 955-966.
- (20) WALKER, R. H., AND BROWN, P. E. 1935 Effects of lime on the hydrogen-ion concentration and base exchange complex of Grundy silt loam. *Iowa Agr. Exp. Sta. Res. Bul.* 178.
- (21) WHITE, J. W. 1917 Relative value of limestone of different degrees of fineness for soil improvement. *Pa. Agr. Exp. Sta. Bul.* 149.

A METHOD OF ESTIMATING THE REACTING RATE OF DIFFERENT PARTICLE SIZES OF LIMESTONE

R. P. THOMAS AND H. M. GROSS

Maryland Agricultural Experiment Station¹

Lime materials have been used for centuries to help supply the basic needs of soils and plants. During this time, many methods have been proposed to evaluate the base-supplying power of the different lime carriers. The recently developed ways of determining the exchange capacity of soils and their degree of saturation with calcium and magnesium afford a very satisfactory estimation of the lime needs of the soil. Such methods are based on the theory that applied lime materials will go readily into solution and replace the exchangeable hydrogen. Since the different lime materials vary greatly in their crystal structure, composition, hardness, and particle sizes, their rate of solubility fluctuates. Consequently, lime materials vary widely in their ability to react with the soil and to supply the lime needs of both soils and plants. Any method, then, that would aid in evaluating the rate of reaction in the soil of the many different kinds of lime particles would be of substantial value.

The need for such a test has been accentuated recently by federal payments for the promotion of lime use. Usually these payments have been based on the ability of the material to supply the immediate lime needs of a soil. As a coarse or less reactive material would be of little immediate value to the farmer, federal aid for such materials is usually less. It would be advantageous to a lime user if he had available an easy way of estimating the surface reaction of his material. At this time there is no easy or satisfactory method of evaluating the many kinds of lime materials.

This paper reports a study of the many methods proposed to evaluate different sizes of lime materials and makes suggestions as to how these methods may be improved.

PREVIOUS WORK

A survey of all the literature pertaining to methods of evaluating solubility and reaction rate of the different particle sizes of lime materials, and even other calcium and magnesium compounds, was made. It has been a common practice for some time to evaluate various particle sizes of agricultural lime materials on the basis of their sieve analysis. In such procedure it was assumed that the reacting surfaces increased as the particle size decreased. Bear and Allen (2) showed such a relationship.

Work of Coleman and Klomme (3) agreed essentially with that of Bear and Allen and also showed that 100-mesh lime material was about as reactive in the soil as the ordinary oxide and hydroxide forms of lime. Later work by Barnes

¹ Miscellaneous publication No. 104, Contribution No. 2268 of the Maryland Agricultural Experiment Station (agronomy department, soils) College Park. The authors are now with International Minerals & Chemical Corporation and Bureau of Reclamation, respectively.

(1) indicated that screen tests for sieve analysis are not always a true estimation of the surface exposed and do not always indicate the rate of reaction of lime materials. He proposed a method of treating a lime sample with strong oxalic acid. The oxalate ions react with the calcium and magnesium ions on the outer surfaces of the lime particles. This method usually gives high results for magnesia limes.

Morgan and Salter (4) studied the solubility of limestone as related to its physical properties. In their work they considered the porosity, hardness, specific gravity, and crystalline structure of lime material in relation to the rates of reaction within the soil. Their work showed no apparent relationship between the rate of solubility in the soil and the physical properties of the lime material. They did, however, obtain a close agreement between the reaction of lime material in acetic acid and lime reaction in the soil. In their study most of the magnesium lime materials were less soluble or reactive than the calcium materials in both acetic acid and soil.

TABLE 1

Influence of different screen sizes of limestone on the reaction with oxalate ions expressed in terms of potassium permanganate

SCREEN SIZE	KMnO ₄ EQUIVALENT OF OXALATE WHICH REACTED WITH SURFACES OF DIFFERENT SIZED PARTICLES OF LIMESTONE	
	High-calcium limestone	High-magnesia limestone
<i>mesh</i>	<i>ml.</i>	<i>ml.</i>
20	2.20	5.50
40	3.35	8.50
60	4.30	12.25
80	4.85	22.50
100	7.43	25.85

It seems from this previous work that a consideration of both the solubility and the surface of the lime particles is necessary for an accurate evaluation of the reaction of the particles.

EXPERIMENTAL WORK

At the start of this investigation two local limestones were selected as standard materials. One was a high-grade calcium limestone containing 48 per cent CaO and 2 per cent MgO. The other was a dolomitic or high-magnesia limestone containing 29 per cent CaO and 16 per cent MgO. Portions of these two materials were screened through the following nest of sieves: 10-20-30-40-50-60-70-80-100-200-mesh. The following separates were washed free of dust: 20 to 30, 40 to 50, 60 to 70, 80 to 100, and 100 to 200. Each of these dust-free separates was run through the procedure proposed by Barnes. A 1-gm. sample of these materials was treated with 5 ml. of saturated oxalic acid. The excess acid was removed, then the oxalate was dissolved with H₂SO₄. The dissolved oxalate was determined by titrating with 0.1 N KMnO₄. The results are given in table 1.

Although these results were somewhat as should be expected for the different particle sizes of the two lime materials, they were not in agreement with each other. The magnesia limestone was far more reactive. As a further check on the differences between these two kinds of lime, other lime samples were similarly treated. Again, the higher magnesia limes always indicated a greater reacting surface, although there was considerable variation for the different lime materials.

In an effort to devise a procedure that would come close to an approximation of the true reactive value of these lime materials in the soil, various procedures and chemical tests were tried. Samples of these standard lime materials were treated with many different types of acids and salts. The acids used were hydrofluoric, phosphoric, acetic, phthalic, stearic, oelic, formic, and oxalic. The salts used were potassium acid phthallate, sodium fluoride, potassium oxalate, and sodium oxalate. Many variations in strengths of solutions, sample sizes, and procedures were tried. None of the tests were equally suitable for the two forms of limestones.

A study was then made of the two methods proposed by Morgan and Salter and by Barnes. Since the Morgan and Salter method was less reactive and the Barnes method more reactive with the magnesia materials, various combinations of acetic and oxalic acid mixtures were tried on these two limestones. Fairly satisfactory results were obtained by some of the acid mixtures. They were not consistent, however, with particle sizes for a wide variety of other lime materials. When the higher concentrations of oxalic acids were used, the magnesia limes continued in their reaction on the steam bath as long as free acid or lime particles were present. The calcium lime reaction with the acids ceased shortly after the lime and acids were mixed.

These observations indicated that the magnesia limestones continued in their reaction with the oxalic acid long after the ions of calcium and magnesium on the surfaces of the crystals had reacted with oxalate ions. The increase of magnesium ions and the decrease of oxalate ions in the solution, as found by qualitative tests, suggested that the magnesium oxalate precipitate gradually dissolved from the surface of lime particles, thus exposing more calcium ions to react with the oxalate ions. These continued reactions between the magnesia limes and the oxalic acid were greater as the concentration of oxalic acid or oxalate ions increased. This probably explains the high results obtained with Barnes' method for the magnesia limestones.

Laboratory test

From these observations it was concluded that if a weaker oxalic acid was used with a greater concentration of lime particles it might be possible to reach a point where the magnesium oxalate ions had a low rate of solubility. After many tests, such a combination was found. This is given in the following procedure, which was quite satisfactory for many lime materials: A 10-gm. sample of the lime material was treated with 100 ml. of 0.1 *N* oxalic acid in an Erlenmeyer flask and allowed to react on the steam bath for an hour. The flasks were

removed and the contents allowed to cool, and then either 10 ml. of the clear liquid was pipetted off or a portion of the liquid was filtered and a 10-ml. aliquot removed. This 10-ml. sample was diluted with 10-15 ml. of water and about 2 ml. of 2 N H_2SO_4 , heated, and titrated with 0.1 N $KMnO_4$. The results of such

TABLE 2

Influence of different particle sizes of limestone on reaction rate with oxalate ions expressed in terms of potassium permanganate and in percentage of oxalate ions reacted

SIEVE SIZE	HIGH-CALCIUM LIMESTONE		HIGH-MAGNESIA LIMESTONE	
	$KMnO_4$ equivalent	Oxalate ions used	$KMnO_4$ equivalent	Oxalate ions used
mesh	ml.	%	ml.	%
20	9.2	8	9.6	4
40	8.0	20	8.4	16
60	5.6	44	6.2	38
80	2.8	72	3.8	62
100	0.2	98	1.5	85

TABLE 3

Influence of different separates of two standard limestones on exchangeable calcium, magnesium, hydrogen, pH, and percentage saturation in soil

SIZE OF LIME SEPARATE ADDED TO SOIL	EXCHANGEABLE CATIONS PER 100 GM. SOIL			CALCIUM AND MAGNESIUM SATURATION	pH OF SOIL
	Calcium	Magnesium	Hydrogen		
High-calcium limestone					
mesh	me.	me.	me.	%	
20	4.94	0.28	6.36	41.1	4.5
40	5.21	0.28	5.38	45.8	4.6
60	7.11	0.31	4.76	55.8	4.9
80	8.96	0.32	4.03	64.4	5.6
100	10.40	0.34	2.97	72.5	6.2
200	12.46	0.36	2.00	80.5	6.7
High-magnesia limestone					
20	3.09	0.47	6.50	31.9	4.5
40	3.91	0.48	5.93	38.4	4.5
60	4.39	0.70	5.35	44.1	4.8
80	4.90	0.86	4.84	49.2	5.0
100	6.28	1.00	3.78	59.8	5.7
200	7.62	1.68	3.05	69.1	6.6

a treatment on the two standard samples of limestone are given in table 2. The $KMnO_4$ -equivalent values are the number of milliliters of $KMnO_4$ required to oxidize the unreacted or unused oxalate ions. The percentage values show the oxalate ions that reacted with the calcium and magnesium ions on the surface of the lime particles (the difference between the 10 ml. of oxalic acid added to the lime sample and the oxalate equivalent of the $KMnO_4$ multiplied by 10).

These data indicate that the coarser lime particles have very little reacting surface or precipitate little of the oxalate ions and that the fine lime particles reacted rapidly with the oxalate ions. The magnesia lime was slightly less reactive than the high-calcium limestone.

Soil tests

To check on the reaction between different particle sizes of lime materials and soil, a series of pot tests were made with Collington fine sandy loam having a pH value of 4.5. The total exchangeable capacity and the millequivalents of

TABLE 4
Standard sieve analysis of limestone samples

SAMPLE NO.	PARTICLE SIZES OF LIMESTONE ACCORDING TO STANDARD MESH SIEVE SIZES										
	10	10-20	20-30	30-40	40-50	50-60	60-70	70-80	80-100	100-200	>200
	%	%	%	%	%	%	%	%	%	%	%
1	90.0	8.0	0.5							0.1	1.4
2	0.1	0.3	0.4	0.7	1.0	1.2	1.4	1.5	7.4	15.0	71.0
3	5.0	26.0	11.0	11.0	8.4	2.6	3.4	3.0	3.0	11.0	15.6
4	6.0	24.0	12.0	11.0	10.0	5.0	4.0	1.8	3.5	10.5	12.2
5	3.2	5.2	9.5	10.0	11.0	5.0	4.0	2.6	4.6	11.4	38.5
6	7.0	24.0	11.0	9.0	6.0	3.0	2.0	1.0	2.1	8.1	27.0
7											100.0
8	17.0	34.0	10.0	7.0	4.0	1.3	1.0	0.6	2.0	7.0	16.0
9	10.0	32.0	10.0	8.0	7.0	4.0	3.0	2.0	2.0	8.0	14.0
10	2.6	47.0	16.0	12.0	2.6	2.9	1.6	1.2	2.2	5.4	7.4
11	3.0	26.0	12.0	11.0	10.0	5.0	3.0	2.0	4.3	13.0	10.0
12	15.0	33.0	10.0	7.4	5.0	2.5	2.0	1.5	2.0	11.6	10.0
13											100.0
14	14.4	22.0	5.2	4.5	3.3	1.2	1.0	1.0	1.4	5.0	41.0
16	27.0	42.0	6.5	6.6	3.6	1.4	1.0	1.0	1.3	3.4	6.2
17	0.3	21.0	10.0	10.0	8.2	3.6	3.0	2.2	4.0	11.3	26.4
18										20.0	80.0
19	17.0	44.0	8.7	8.4	5.3	2.3	1.5	1.1	1.8	3.2	6.7
20	0.2	5.0	5.8	9.3	11.2	6.0	5.6	4.2	8.0	17.0	28.7
21										20.0	80.0
22*											100.0

* Hydrated lime.

calcium, magnesium, potassium, manganese, and hydrogen were determined in this soil. From these data were calculated the amount of calcium and magnesium that would be needed to displace the hydrogen from the exchange complex or neutralize the soil acid. The two standard lime samples were applied at the rate of 100 per cent hydrogen-ion replacement. All treatments were run in duplicate. The pots were incubated and kept moist for 3 months with occasional mixing. Each pot of soil was then sampled, and the pH value, exchangeable calcium, magnesium, and hydrogen were determined. These data are recorded in table 3. Only the results with the 100 per cent rate of liming are reported here.

Table 3 shows that in the 3-month period not all of the lime had reacted. Qualitative tests indicated that there were some free carbonates even in the soil receiving the finest material. The coarser material showed little reaction with the soil colloids, as it had not changed the pH value or the exchangeable hydrogen and calcium. These data show also that the magnesia limestone used in these pot tests reacted less with the soil than did the high-calcium limestone. It was about 80 per cent as effective as high-calcium lime material in neutraliz-

TABLE 5

Influence of different sources of limestone and particle sizes on their reaction with oxalate ions expressed in terms of potassium permanganate and as effective reaction percentage

SAMPLE NO.	COMPOSITION OF LIMESTONE		KMnO ₄ VALUE OF REACTED OXALATE IONS							REACTION OF LIME MATERIALS
	CaO	MgO	Un-screened	20-mesh	40-mesh	60-mesh	80-mesh	100-mesh	200-mesh	
	%	%	ml.	ml.	ml.	ml.	ml.	ml.	ml.	%
1	51.9	0.7	5.8	9.0	6.6				0.1	42
2	47.8	0.8	0.2							98
3	54.3	0.8	2.0	8.5	5.9	4.3	2.8	2.3	1.5	80
4	30.0	21.5	1.0	8.0	5.0	3.4	1.8	1.1	0.2	90
5	50.7	2.5	2.5							75
6	52.8	0.9	2.0	8.9	6.3	5.1	4.0	2.2	0.2	80
7	53.7	0.7	0.1							99
8	53.7	0.7	0.2	6.8	1.7	1.2	0.5	0.2	0.1	98
9	53.7	0.7	2.0	9.2	5.8	2.0	1.5	0.8	0.5	80
10	30.0	20.0	4.1							59
11	30.0	20.0	3.9	6.3	5.2	4.8	4.0	3.6	3.2	61
12	45.8	2.6	4.0	7.0	4.2	2.8	0.7	0.2	0.1	60
13	45.8	2.6	0.1							99
14	53.8	1.0	0.1							99
16	30.0	19.5	3.2							68
17	30.0	19.5	2.2							78
18	30.0	19.5	1.8							82
19	53.7	1.1	0.5							95
20	53.7	1.1	0.1							99
21	53.7	1.1	0.1							99
22	46.5	31.0	0*							100

* Hydrated lime.

ing the soil. This is somewhat in agreement with the work reported by other investigators (5). These data indicate less reactive surface for this magnesia limestone than for the high-calcium limestone. The results with the two standard samples (table 2) were in this order.

Tests on limestones

A trial of the proposed procedure was made on 21 lime samples sent in by different companies. These samples were selected because of their variation in sieve and chemical analyses. The analyses obtained with a standard rotating

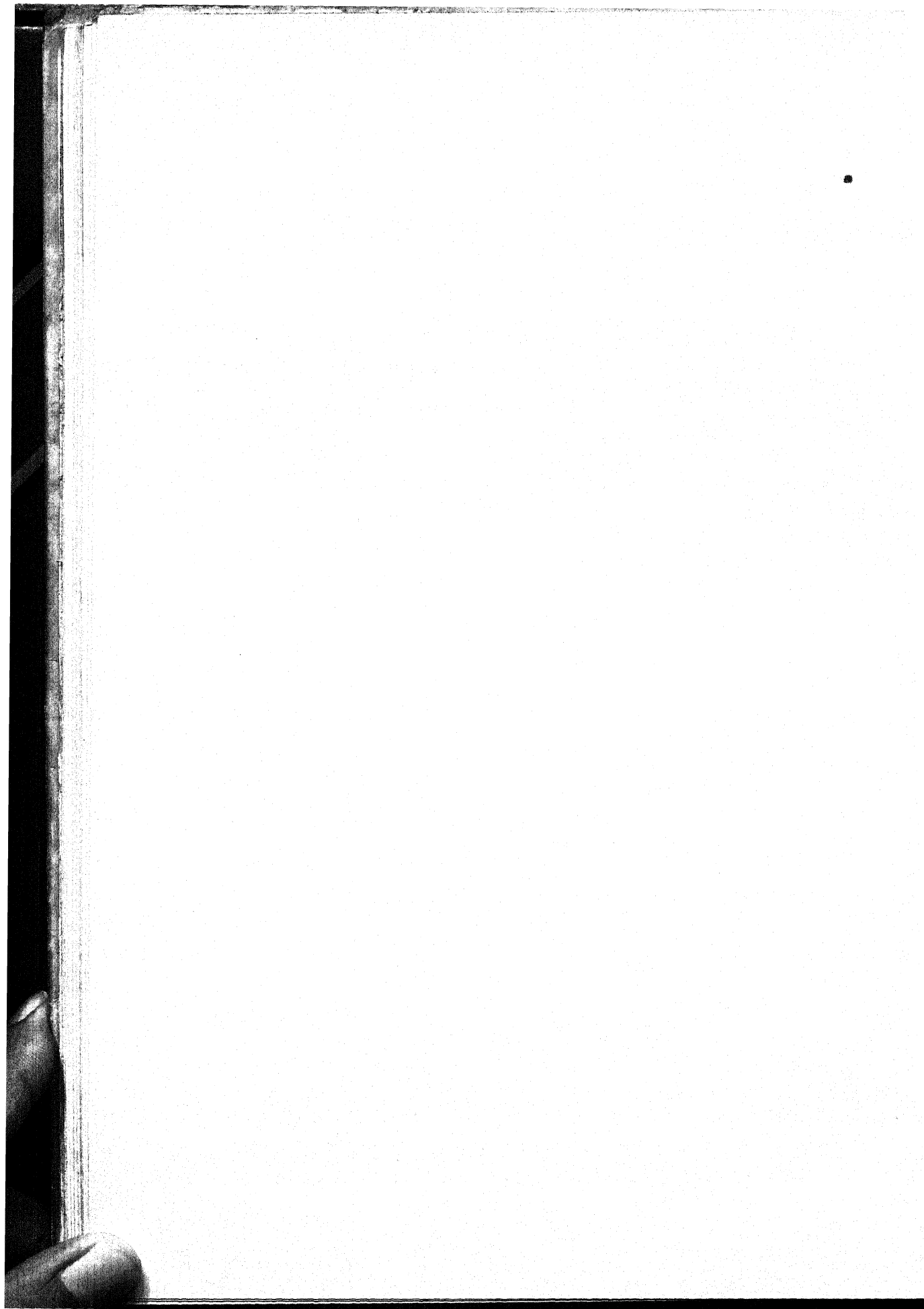
tap sieving machine are shown in table 4. Results of the proposed procedure on the 21 samples are given in table 5. The titration values for unscreened, as well as sieve separates, are also shown in this table. The coarse lime was not nearly so reactive, whereas the fine limes were almost 100 per cent reactive by this procedure. Some of the high-magnesia limes were as reactive as some of the high-calcium samples. In other instances the high-calcium limes were more reactive than the magnesia materials. These results seem to be somewhat in line with the results reported by Salter *et al.* (4, 5) in regard to the effectiveness of different lime materials in neutralizing soils. Although more pot tests with many soils and limestones and subsequent laboratory tests are needed, it is believed that the proposed simple laboratory procedure offers considerable promise as a means of evaluating different particle sized limestones. The 10-gm. sample of limestone permits a better representation of lime materials than a 1-gm. or 2-gm. sample.

SUMMARY

Many requests for a method of evaluating the reaction rate in a soil of lime particles of different degrees of fineness initiated this study. A revision of the method suggested by Barnes seemed quite satisfactory. The revised procedure consists of treating 10 gm. of lime material with 100 ml. of 0.1 *N* oxalic acid, heating on the steam bath for an hour, cooling, taking a 10-ml. clear liquid aliquot and titrating with 10 ml. *N* KMnO_4 . The relative efficiency of this simple method can be easily expressed as a percentage value. An easy way of evaluating the surface reaction of different particle sizes of limestone is proposed.

REFERENCES

- (1) BARNES, E. E. 1947 A new method for estimating the surface of liming materials and other insoluble calcium compounds. *Soil Sci.* 63: 285-289.
- (2) BEAR, F. E., AND ALLEN, L. 1932 Relation between fineness of limestone particles and their rate of solution. *Indus. and Engin. Chem.* 24: 998-1001.
- (3) COLEMAN, O. T., AND KLOMME, A. W. 1941 Liming Missouri's soils. Missouri Agr. Exp. Sta. Cir. 218.
- (4) MORGAN, M. F., AND SALTER, R. M. 1923 Solubility of limestones as related to their physical properties. *Soil Sci.* 16: 293-305.
- (5) SCHOLLENBERGER, C. J., AND SALTER, R. M. 1943 A chart for evaluating limestone. *Jour. Amer. Soc. Agron.* 35: 955-966.



INFLUENCE OF LIMING MATERIALS ON pH VALUES OF SIX MARYLAND SOILS

J. H. HOYERT AND J. H. AXLEY

Maryland Agricultural Experiment Station¹

The State of Maryland used 219,901 tons (2) of liming material in 1949. On the basis of past experience it has been estimated that lime consumption in Maryland should be approximately doubled. To increase the consumption of liming materials, it is necessary to show the farmer the benefits of liming. If a more efficient system of liming soils can be found, the farmer will be more easily convinced of the value of lime. This is a report on an investigation of the influence of various important liming materials on the pH values of six prominent soils of Maryland and is intended as a reference for Maryland agricultural workers in recommending liming practices.

MATERIALS AND METHODS

Soil types

Soils representative of the important agricultural areas of the state were chosen. These soils differed considerably in profile characteristics. Seven fields of six different types were selected. These were Mattapex silt loam, Matawan sandy loam at two different locations, Sassafras silt loam, Chester silt loam, Duffield silt loam, and Emory silt loam.

Liming materials

Three chemical forms of agricultural liming materials were used. The first form was ground limestone, which was chosen because it is the major liming material used in Maryland and could be obtained in varying degrees of fineness. The second and third forms were burnt lime and hydrated lime respectively. This study included three grades of the ground limestone with sieve analyses as shown in table 1. These limestones are typical of the fineness grades used in the state.

Determination of quantities of lime applied

Bray and DeTurk (3) found that the sum of the calcium and magnesium on the exchange complex was approximately 80 per cent of the total exchange capacity of soil near neutrality. As a starting point in this experiment this criterion was assumed to be the optimum condition. Thus, based on the chemical analysis of the untreated soil and on the assumption of the complete solubility of the lime and adsorption by the soil colloids, the amount of lime neces-

¹ Paper No. A321, Contribution No. 2281 of the Maryland Agricultural Experiment Station (department of agronomy). Part of dissertation submitted by the senior author (now at Edisto Experiment Station, S. C.) in partial fulfillment of the requirements for the degree of doctor of philosophy. The authors express their appreciation to R. P. Thomas, who directed the field phase of this study; to E. Strickling for his many helpful criticisms; and to H. B. Winant for his invaluable aid.

sary to attain an 80 per cent calcium plus magnesium saturation of the total exchange capacity was applied. Likewise, in a second treatment, enough lime to give a 160 per cent saturation of the total exchange capacity was applied. This gave two levels of chemically equivalent weights of the various materials so that the effect of quantity could be observed on the soil. The exchange complex of

TABLE 1
Sieve analyses of the three grades of ground limestone

GRADE	PERCENTAGE OF LIMESTONE RETAINED ON DIFFERENT SCREEN SIZES*							
	6-mesh	10-mesh	35-mesh	65-mesh	100-mesh	150-mesh	200-mesh	Through 200 mesh
Medium I.....	0	16.69	42.77	13.67	4.40	—	5.78	16.82
Medium II.....	0	14.80	39.80	12.90	4.82	—	7.38	20.18
Fine.....	0	0	1.22	16.90	12.95	16.75	15.16	37.00

* U. S. standard sieve series.

TABLE 2
Amount of each lime material in light and heavy application rates in tons per acre

SOIL TYPE	LIME MATERIAL					
	Rate of Application	Med. I limestone	Med. II limestone	Fine limestone	Burnt lime	Hydrated lime
Mattapex silt loam	Light	1.65	1.70	1.75	1.15	1.20
	Heavy	4.35	4.40	4.80	3.00	3.15
Matawan sandy loam (Salisbury)	Light	0.62	0.62	0.62	0.43	0.50
	Heavy	2.25	2.25	2.25	1.55	1.80
Matawan sandy loam (Cordova)	Light	0.85	0.85	0.85	0.47	0.67
	Heavy	2.78	2.78	2.78	1.71	2.18
Sassafras silt loam	Light	1.15	1.15	1.15	0.70	0.95
	Heavy	3.65	3.65	3.65	2.25	2.85
Chester silt loam	Light	0.68	0.68	0.68	0.42	0.53
	Heavy	4.55	4.55	4.55	2.75	3.85
Duffield silt loam	Light*					
	Heavy	3.95	3.95	3.95	2.40	3.05
Emory silt loam	Light*					
	Heavy	4.05	4.15	4.45	2.80	2.90

* No lime required at this level.

Emory and Duffield silt loams was already 80 per cent saturated. On these soils the lighter treatments were omitted. Table 2 presents the amounts of liming materials applied to each soil.

Experimental plots

Eleven plots, composed of a check plot plus five lime treatments each at two rates, were set up on each of the seven fields. These plots were 14 feet wide and

31 feet long, approximately 0.01 acre. At each location complete blocks were used without replication.

The lime materials were broadcast by hand on the plots in the spring of 1947.

Soil sampling procedure

Representative soil samples were collected 2 to 4 months, 1 year, 2 years, and 3 years after liming. Samples were taken at a depth of 0-6 inches (1).

Laboratory procedure

The soil samples were air-dried, passed through a 10-mesh sieve, and mixed to give uniformity. The pH values were determined with a Beckman pH meter using a 2:1 soil to water ratio as outlined by Mason and Obenshain (5). Duplicate analyses were made on each sample.

TABLE 3

Effect of light lime applications on pH values compiled for all sampling dates as averaged for Mattapex, Matawan (Salisbury and Cordova), Sassafras, and Chester soil series

TREATMENTS	pH VALUE				
	2 to 4 months	1 Year	2 Years	3 Years	Average
Medium I limestone.....	5.78	5.94	5.92	6.10	5.94
Medium II limestone.....	6.04	6.08	5.98	5.98	6.02
Fine limestone.....	6.14	6.14	6.22	6.22	6.18
Burnt lime.....	6.16	6.06	6.06	5.92	6.05
Hydrated lime.....	6.18	6.12	6.06	6.30	6.17
Untreated.....	5.64	5.68	5.66	5.72	5.68

Significant difference between treatments, 0.15; no significant difference between dates.

RESULTS

The effects of the light lime applications are summarized in table 3. These data show the influence of the different liming treatments and the effect of time on the pH value of the surface soils. All the liming materials increased the soil pH values significantly above the values of the untreated plots. Also the hydrated and fine limestone treatments showed a significantly higher soil pH than the Medium I and Medium II limestones. Burnt lime gave a lower soil pH than did the hydrated and fine limestones but higher than did the medium I and medium II limestone. Otherwise, the effect was not significantly different from that of any other treatment. There was no significant difference between the soil reaction at the different sampling dates.

The influence of the heavy lime applications are summarized in table 4. All liming materials significantly increased the soil pH. The hydrated lime gave a significant increase in soil pH over the three limestone treatments, but not over the burnt lime. Although burnt lime tended to increase the soil pH above the values from the limestone treatments, this increase was not significant. The influence of degree of fineness of limestone was not significant.

No significant difference was shown between soil pH measurements after the

first 2 to 4 months and after 1 year. After 2 years, however, a significant decrease occurred. This decrease was believed to be a seasonal variation. At the end of 3 years the soil reaction was significantly higher than at all previous sampling dates.

TABLE 4

Effect of heavy lime application on pH values compiled for all sampling dates as averaged for Mattapez, Matawan (Cordova), Sassafra, Chester, Duffield, and Emory soil series

TREATMENTS	pH VALUE				
	2 to 4 Months	1 Year	2 Years	3 Years	Average
Medium I limestone.....	6.43	6.72	6.32	6.55	6.50
Medium II limestone.....	6.45	6.75	6.37	6.78	6.59
Fine limestone.....	6.50	6.55	6.52	6.92	6.62
Burnt lime.....	6.70	6.78	6.62	6.87	6.74
Hydrated lime.....	7.18	6.85	6.53	7.40	6.99
Untreated.....	5.83	6.02	5.87	5.90	5.90
Average for date.....	6.52	6.61	6.37	6.74	

Significant difference between treatments, 0.28; between dates, 0.12.

DISCUSSION

Soil reaction

Lime treatments employed in this investigation increased the soil pH significantly above the values of the untreated plots. As would be expected from the law of mass action, each of the soils showed a larger pH increase from the heavier lime applications. In general, not much difference was shown within the different lime treatments except in the hydrated lime. The reason for the greater action of the hydrated form is probably twofold: the hydrated lime is more soluble than the carbonate form, and its extremely fine state of division provides a larger effective surface area.

Burnt lime did not tend to change the pH values so much as did the hydrated form, although the difference was not statistically significant. This trend was thought to be due to the greater degree of fineness of the hydrated lime and the tendency of the burnt lime to aggregate, or plaster itself into larger particles, when it came in contact with the moist soil. A comparison of heavy applications of burnt lime and the limestones generally showed greater pH changes for the burnt lime, but the differences were not statistically significant. This effect on pH was attributed to the greater solubility of burnt lime.

Only the light application of fine limestone gave a significant pH increase when compared with the coarser limestones. In general, however, there was a trend toward a slightly greater increase in pH value with an increase in the state of division. This could be predicted on the basis of the increased solubility resulting from the larger surface area. The source of the fine limestone was different from that of the Medium I and Medium II limestones, and for this reason a possible solubility difference might exist.

The work of Lyon (4) and White (10) might indicate that the degree of fineness has a greater effect upon the pH change than our experimental data for the heavier lime applications exhibit. This difference might be explained by the sieve size analysis of the three limestones (table 1). The Medium I and Medium II limestones are too similar in analysis to give an extensive difference. In all three grades of limestone, there was a large amount of the finest portion, which passes through a 200-mesh sieve. This is believed to be the situation encountered by the farmer when he purchases better grades of ground limestone. When these limestones were applied to the soil in large quantities, as in this experiment, there was a sufficient quantity of this finer material to react with the soil system and thus produce somewhat similar results in the pH. In investigations upon the effect of fineness of limestone, such as Lyon's study, the limestones were screened so that each tested material was all of the same approximate diameter. When compared with another size range of limestone, these sieve separates gave an appreciable difference in pH value of a soil.

The small differences between the different grades of limestones indicate that it might not always be necessary to grind limestone very fine. If a limestone which is ground to pass a 20- or 40-mesh sieve contains enough fine material to give approximately the same immediate soil pH effect as that which is ground to pass a 100-mesh sieve, then this coarser material might be superior, since it is thought to persist in the soil over a longer period. The results suggest the need for further experimental work.

The changes in soil pH between sampling dates were small and probably of little agronomic significance. The greatest change in soil reaction occurred within the first 4 months after liming under the conditions of this experiment.

The fact that only small differences in effect on the soil were shown between the various lime materials indicates that the prime consideration of a farmer in choosing a liming material should be the cost per unit of neutralizing power. When lime materials are applied for crops demanding a high pH value and quick results are desired, then the finely divided and more readily soluble hydrated lime would probably be the most nearly ideal.

Adequacy of lime recommendations

A soil pH of 6.5 is usually considered optimum for general farming, and most lime recommendations are designed to raise the pH to approximately this level. Table 5 shows the type of chart used by some states in advising farmers of the approximate amounts of limestone required.

It was thought that in many cases inadequate amounts of lime were being recommended. Although the amounts added in this investigation were not exactly the same as those recommended in table 5, they were close enough to serve as a test of the adequacy of the recommendations under Maryland conditions. Table 6 gives the soil pH values 1 year after the treatments.

Table 6 indicates that in five of the seven soils the recommended amounts of lime in table 5 did not raise the soil pH to the expected 6.5 value. Where 6.5 was reached, the original soil pH exceeded 6.0. Seemingly the limestones reacted

relatively slowly with these acid soils and larger amounts should be used to compensate for this.

Use of a compensating factor will give a more adequate lime recommendation chart for these acid soils. Such a factor was determined from measurements of the exchangeable hydrogen before and after limestone treatments. It was found that 2,000 pounds of the limestones per acre, rather than 1,000 pounds, was needed to replace 1 me. of exchangeable hydrogen per 100 gm. of the soils studied.

TABLE 5
*Lime required by different soil types to attain a pH of 6.5**

pH OF UNLIMED SOILS	LIMESTONE RECOMMENDED PER ACRE		
	Sandy loam soils	Loam soils	Silt loam soils
	<i>ton</i>	<i>ton</i>	<i>ton</i>
4.8	1.70	3.00	4.25
5.0	1.50	2.70	3.75
5.5	1.00	1.80	2.50
6.0	0.50	0.90	1.25

* Calculated from Pettinger, N. A. A useful chart for teaching the relation of soil reaction to the availability of plant nutrients to crops. Va. Agri. Exp. Sta. Bul. 136. 1935.

TABLE 6
*Results of recommended applications of limestone on pH values of different soil types in Maryland**

SOIL TYPE	pH OF UNLIMED SOIL	AMOUNT OF LIME RECOMMENDED PER ACRE	AMOUNT OF LIME ADDED PER ACRE	RESULTING SOIL pH AFTER 1 YEAR
		<i>ton</i>	<i>ton</i>	
Sandy loam.....	5.63	1.00	0.85	5.84
Sandy loam.....	4.95	1.50	1.47	5.34
Sandy loam.....	6.40	0.10	0.60	6.61
Silt loam.....	5.45	2.50	3.65	6.34
Silt loam.....	5.47	2.50	4.90	6.00
Silt loam.....	4.83	4.25	4.40	5.47
Silt loam.....	6.08	1.00	0.68	6.58

* Values are from an average of 12 plots on each soil type.

This factor, combined with an estimate of the exchangeable hydrogen, was used to devise a chart of lime recommendations applicable to these soils.

The relationship between the pH value of a soil and its corresponding percentage hydrogen saturation of the exchange complex was used as a basis for estimating the exchangeable hydrogen. That a relationship between pH value and percentage base saturation exists for any one soil has been shown by Pierre and Scarseth (9), Merkle (7), Mehlich (6), and Peech (8). Pierre and Scarseth and Mehlich have concluded that soils of different mineral composition but with the same pH value could vary considerably in their percentage base saturation.

In many of the soils in Maryland a linear relation holds between the soil pH and its percentage hydrogen saturation. The closeness of this relationship is indicated by figure 1, in which data for 24 soil types from 34 different locations are plotted. The equation for the regression of soil pH value on the percentage

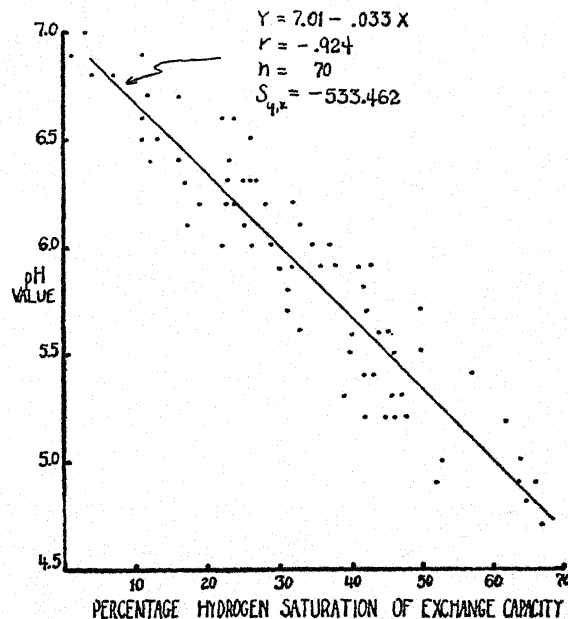


FIG. 1. RELATIONSHIP BETWEEN pH AND PERCENTAGE HYDROGEN SATURATION OF 24 MARYLAND SOIL TYPES FROM 34 LOCATIONS

TABLE 7

Approximate amounts of limestone recommended for different soil types of Maryland to attain a pH of 6.5

pH OF UNLIMED SOILS	LIMESTONE RECOMMENDED PER ACRE		
	Sandy loam soils	Silt loam soils	Silty clay loam soils
	<i>ton</i>	<i>ton</i>	<i>ton</i>
4.8	2.50	4.00	6.00
5.0	2.25	3.60	5.40
5.5	1.50	2.40	3.60
6.0	0.75	1.20	1.80

hydrogen saturation is $Y = 7.01 - 0.033 X$, where Y is the soil pH value and X is the percentage hydrogen saturation. The correlation coefficient for these values is -0.924 .

An estimate of the exchangeable hydrogen was obtained by multiplying the percentage hydrogen saturation in figure 1 by the total exchange capacity of the soil: for example, if a soil with a pH value of 6.0 has an exchange capacity of

10 me. per 100 gm., 30 per cent of its exchange capacity, or 3 me., is exchangeable hydrogen.

The estimated exchangeable hydrogen of a soil and the amount of lime needed to neutralize this hydrogen (2,000 pounds per acre to replace 1 me. of exchangeable hydrogen) provided a reasonably accurate recommendation of the lime needed to raise the soil pH to a desired level. Table 7 shows adequate amounts of lime to raise to 6.5 the pH of a soil which fits the relationship in figure 1.

SUMMARY AND CONCLUSIONS

The influence of various liming materials on pH values was studied on six important Maryland soils. These soils were in prominent agricultural areas throughout the state and represent diversified conditions. Five different liming materials—Medium I limestone, Medium II limestone, fine limestone, burnt lime, and hydrated lime—at two weight levels were included in the study. The effect of time on the pH values of limed soils was also studied over a 3-year period.

The following general conclusions were drawn:

The pH values of the surface soil was significantly increased by all additions of lime materials.

The hydrated form of lime produced the greatest effect on the soil reaction.

No significant differences in soil pH were shown between the different grades of fineness of limestone in the heavier applications used.

The pH values of soils treated with light applications of fine limestone were increased more than were those of soils treated with the coarse limestones.

Increasing the quantity of liming material added to the soil increased the pH value more than did the greater degree of fineness.

The greatest change in soil reaction occurred during the first 2 to 4 months after treatment.

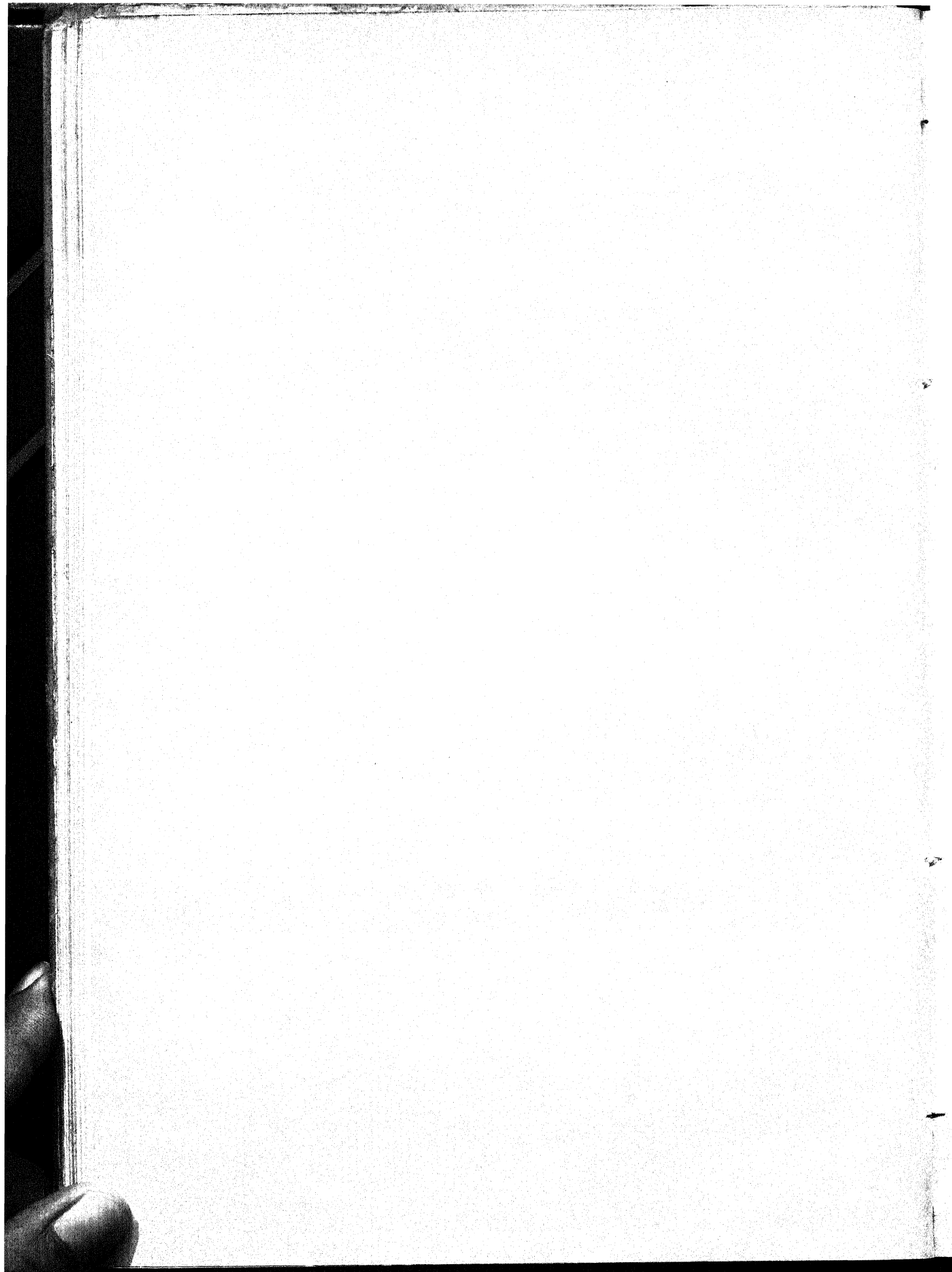
Although the five lime materials showed only slight differences in effect on soil reaction, the following general trend in order of increasing effect was noted: Medium I limestone, Medium II limestone, fine limestone, burnt lime and hydrated lime.

Lime recommendations for Maryland soils should be increased. A chart showing amounts of limestone necessary to raise the soil pH to the desired value of 6.5 is included.

REFERENCES

- (1) Association of Official Agricultural Chemists 1945 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.
- (2) BOPST, L. E. 1950 Maryland lime facts for 1949. State Inspection and Regulatory Service, University of Maryland, College Park.
- (3) BRAY, R. H., AND DETURK, E. E. 1931 Field method for lime requirements of soils. *Soil Sci* 32: 329-341.
- (4) LYON, T. L. 1931 Relative effectiveness of limestone particles of different sizes. *N. Y. (Cornell) Agr. Exp. Sta. Bul.* 531: 1-16.
- (5) MASON, D. D., AND OBENSHAIN, O. E. 1939 Comparison of methods for determination of soil reaction. *Soil Sci. Soc. Amer. Proc.* (1938) 3: 128-137.

- (6) MEHLICH, A. 1942 Base unsaturation and pH in relation to soil type. *Soil Sci. Soc. Amer. Proc.* (1941) 6: 150-156.
- (7) MERKLE, F. G. 1934 Base exchange studies on the Pennsylvania Jordon field plots. *Soil Sci.* 38: 37-64.
- (8) PEECH, M. 1941 Availability of ions in light sandy soils as affected by soil reaction. *Soil Sci.* 51: 473-486.
- (9) PIERRE, W. H., AND SCARSETH, G. D. 1931 Determination of the percentage base saturation of soils and its value in different soils at definite pH values. *Soil Sci.* 31: 99-114.
- (10) WHITE, J. W., AND GARDNER, F. D. 1918 Relative value of limestone of different degrees of fineness for soil improvement. *Pa. Agr. Exp. Sta. Bul.* 152: 19-27.



INFLUENCE OF PLACEMENT OF LIME COMPOUNDS ON ROOT DEVELOPMENT AND SOIL CHARACTERISTICS

D. LONGENECKER AND F. G. MERKLE

Pennsylvania Agricultural Experiment Station¹

On soils that have been repeatedly limed, the cultural operations have rather thoroughly mixed the residual fragments throughout the entire plowed portion. On soils that have never been limed or have been inadequately limed, certain practical questions arise: Is it sufficient to apply lime at the surface and let it filter and diffuse into the soil below? Is it sufficient to apply the lime in bands near the seed, as fertilizers are commonly applied? What is the function of lime in soils; is it to supply the element calcium or magnesium for nutritional purposes, or does it, in addition, inactivate certain toxic substances and increase the availability of others? In short, should lime be mixed throughout the entire soil stratum in which roots are to develop, or should it be accessible to certain roots only? Does lime diffuse rapidly or slowly through soils? A pot experiment was designed to provide answers to some of these questions.

MATERIALS AND METHODS

An acid soil having a pH value of 4.00 and a lime requirement of 7,600 pounds of CaCO_3 was chosen for this study. It was very low in exchangeable nutrients and high in soluble Al and Mn. Each pot was filled to a depth of 9 inches and contained the equivalent of 10,500 gm. of air-dry soil. The fertilizer treatments consisted of 75 pounds of N, 150 of P_2O_5 , 100 of K_2O and 50 of MgO per acre applied as NaNO_3 , KH_2PO_4 , and MgSO_4 . All fertilizers were pulverized to pass a 100-mesh screen and were well mixed into the soil. A calcitic limestone, 97.65 per cent of CaCO_3 , was used as the source of lime. Wherever it was used, enough was applied to satisfy the lime requirement of the particular zone to which it was added. The placements were as follows:

Pot 1. The entire pot was fertilized but unlimed.

Pot 3. The entire pot was fertilized and limed.

Pot 5. The entire pot was fertilized. The soil on one side of the pot was limed and that on the other side left unlimed.

Pot 6. The entire pot was fertilized; only the top 3 inches was limed.

Pot 7. The entire pot was fertilized; only the top 6 inches was limed.

Pot 8. Only the lower 6 inches was fertilized and limed.

Pot 9. Only the top and bottom 3-inch layers were fertilized and limed.

Pot 10. The entire pot was fertilized, and areas 2 inches in diameter and 1 inch deep around each seed were limed.

Crimson clover was the test crop. When mature, it was harvested, dried, and weighed. The root systems were carefully removed, washed, dried, and photographed. Samples of soil were removed from the limed and unlimed areas in each pot and examined for the common nutrient and nonnutrient ions.

¹ Contribution from the department of agronomy of The Pennsylvania State College. Paper No. 1687 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

RESULTS

Germination was good. All seeds emerged in 5 days, and but little difference was detectable the first week. By the end of the third week, definite differences in growth were discernible. In the two treatments containing no lime in contact with germinating seeds, pot 8 and the unlimed side of pot 5, the plants were definitely stunted.

The yields of crimson clover and the analyses of the soils made at the close of the growth period are given in table 1. The top growth and root development are shown in figure 1.

TABLE 1
Influence of lime placement on yields of crimson clover and on analyses of soil by zones

APPLICATION	YIELD OF CLOVER PER POT	pH	REPLACEABLE ELEMENTS IN SOIL AT CLOSE OF EXPERIMENT*					
			P	K	Ca	Mg	Al	Mn
	gm.		lb.	lb.	lb.	lb.	lb.	lb.
1. Entire pot, NPKMg no Ca	0	3.8	2	250	500	tr.	45	53
3. Entire pot, NPKMg Ca	72	6.8	5	175	3000	32	4	3
5. Left side, NPKMg no Ca	2	4.1	3	237	350	tr.	37	35
Right side, NPKMg Ca	42	6.6	3	200	2500	37	4	tr.
6. Top 3 inches, NPKMg Ca	72	6.9	15	225	2700	65	tr.	tr.
Bottom 6 inches, NPKMg no Ca		4.4	tr.	200	500	tr.	40	47
7. Top 6 inches, NPKMg Ca	76	6.8	17	100	2700	80	2	2
Bottom 3 inches, NPKMg no Ca		4.4	tr.	150	450	25	45	37
8. Top 3 inches, no fertilizer or Ca	59	4.5	1	150	450	12	37	40
Bottom 6 inches, NPKMg Ca		6.7	5	167	2500	125	5	10
9. Top 3 inches, NPKMg Ca	66	6.7	22	200	2500	250	25	5
Middle 3 inches, no fertilizer or Ca		4.4	tr.	187	250	25	67	50
Bottom 3 inches, NPKMg Ca		6.6	1	137	2700	tr.	10	6
10. Entire 9 inches, NPKMg no Ca	35	4.2	1	150	350	50	50	37
Cores 1 inch, around seed Ca†								

* 2,000,000-pound basis.

† Residual cores not sampled.

Treatment 5 produced good growth on the limed side but almost no growth on the unlimed side. Despite absence of any barrier between the two sides and maintenance of the moisture content at optimum, there was no appreciable movement of salts or growth of roots from one side to the other. The yield and the soil analyses on the unlimed side were similar to those in pot 1. The yield and soil analyses on the limed side were similar to those in pot 3. The low pH and high aluminum and manganese appear to be the causes of the failure of crimson clover to develop on the unlimed side of the container.

Treatment 6 produced a satisfactory growth, but development of fibrous roots was restricted largely to the limed zone, where the soil structure was definitely improved. Soil analyses at the close of the growth period reveal a sharp contrast between the limed and unlimed zones in pH value, available phosphate, Ca, Mg,

Al, and Mn. This suggests very little diffusion of nutrient and toxic ions from zone to zone. The soil analyses for treatment 7 at the close of the experiment reveal the same tendencies between zones that were observed in treatment 6. Figure 1 reveals a deeper development of fibrous roots in pot 7. Soil structure improvement likewise was pronounced in the upper 6 inches, compared with the lower 3 inches. Even though the yield of tops was not markedly better with the 6-inch liming than with the 3-inch, the deeper roots resulting from treatment 7 would undoubtedly enable the crop, under field conditions, to endure drought and utilize soil resources better.

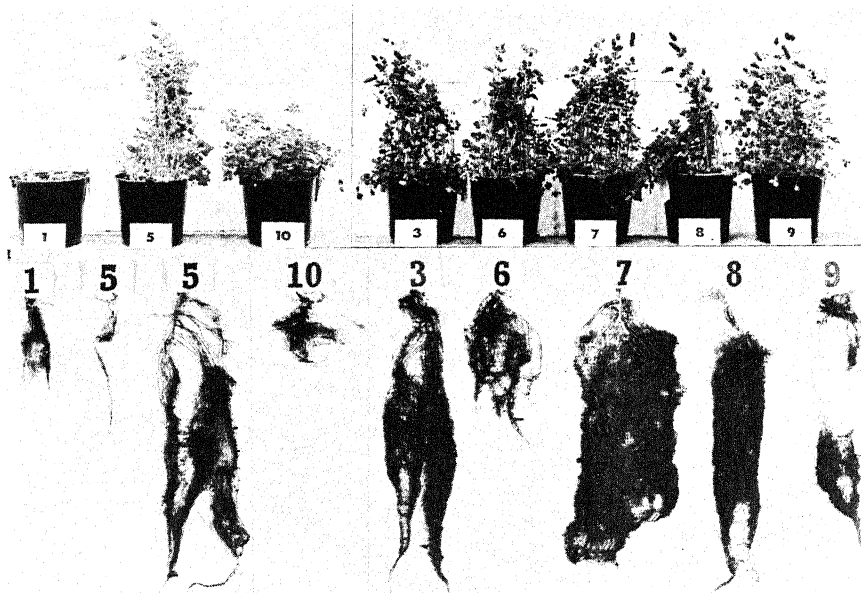


FIG. 1. INFLUENCE OF LIME PLACEMENT ON YIELDS AND ROOT DEVELOPMENT OF CRIMSON CLOVER

1, Unlimed; 5, left, unlimed, right, limed; 10, limed only in cores around seed; 3, limed; 6, limed only in top 3 inches; 7, limed only in top 6 inches; 8, limed only in lower 6 inches; 9, limed only in top and bottom 3-inch layers.

In treatment 8, nutrient and lime deficiencies or toxic substances in the upper 3 inches resulted in a slower start, a smaller final yield, and a root system showing very few fibrous roots in the upper 3 inches but plenty in the lower 6 inches. Soil analyses reveal the reasons. Abundant fibrous roots, a good soil structure, and healthy nodulation existed only in the treated lower 6 inches.

In treatment 9, abundant fibrous roots developed in the treated upper and lower 3 inches, whereas naked connecting strands extended through the untreated middle zone. Soil structure and nodulation improved in the upper and lower zones only. Apparently, primary roots can extend through zones of unfavorable conditions, but development of fibrous branches is dependent upon

the right conditions. Soil analyses show that the middle zone was very slightly influenced by the presence of a limed zone above and below. During growth, all water was applied at the surface and there must have been vertical movement; nevertheless, there has been no very noticeable movement of calcium as shown by the pH value, the replaceable Ca, Al, and Mn.

In treatment 10, seeds germinated well in the limed cores, but soon the plants showed stunting. The yield was half that of the fully limed pots and the root system extended only a short distance outside the limed cores (fig. 3). Analyses of the soil exclusive of the limed cores show that the soil was similar to that of the original unlimed pot 1. This would suggest that germination and early growth might be promoted by drilling lime with the seed but that ultimate yield, drought resistance, and duration of stand would be determined by how thoroughly the entire surface soil was neutralized.

CONCLUSIONS

These experiments lend strong support to the belief that the chief function of liming is to decrease the solubility of aluminum and manganese and possibly to increase the availability of phosphate. They support the belief that neutralization of soil acidity takes place close to the dissolving particles and that calcium does not diffuse rapidly from place to place in soils held at optimum moisture content. They also support the concept that for reasonably rapid results lime compounds should be thoroughly mixed mechanically into the entire soil zone in which roots are expected to develop.

INFLUENCE OF FORM, FINENESS, AND AMOUNT OF LIMESTONE ON PLANT DEVELOPMENT AND CERTAIN SOIL CHARACTERISTICS

R. L. BEACHER, D. LONGENECKER, AND F. G. MERKLE

Pennsylvania Agricultural Experiment Station¹

There is much evidence in the literature that limestone should be finely ground for immediate effectiveness. Two questions of considerable practical importance have not heretofore been adequately investigated: First, will coarse material become effective in future seasons? Second, would use of large amounts of coarse material be feasible and, if so, how much would be needed to equal the fine product in effectiveness? The purpose of this paper is to present evidence obtained on these questions in a series of greenhouse experiments.

MATERIALS AND GENERAL METHODS

Pot tests were set up on Westmoreland silt loam having a pH value of 4.0 and a lime requirement of 7,600 pounds of CaCO_3 . All pots were fertilized with the equivalent of 75 pounds N, 150 pounds available P_2O_5 , 75 pounds K_2O , and 50 pounds MgO per acre in the forms of NaNO_3 , superphosphate, KCl , and MgSO_4 . Where lime was used, calcitic or dolomitic limestone separates or their hydrates were uniformly mixed into the soil. The separates, except the 100-mesh, were first washed with water to remove adhering fine material.

Crimson clover was the primary test crop. The soil was extracted with 0.5 N sodium acetate for analysis.

EXPERIMENT 1—IMMEDIATE AND RESIDUAL EFFECTS OF LIME

Calcitic and dolomitic lime of different degrees of fineness were used in amounts equivalent to the lime requirement of the soil (table 1). When the crimson clover had germinated, 3 weeks after incorporation of the lime and fertilizer, the soil in each pot was sampled and analyzed. When the clover was mature, about 6 months after the soil treatments, it was harvested and weighed, and the soil was again sampled and analyzed. A second application of fertilizer but not of lime was made to each pot. Alfalfa was then grown to measure the residual value of the lime separates. The yields and treatments are shown in table 1 and figure 1.

The crimson clover made no growth when lime was omitted or when 20-40-mesh calcitic or dolomitic limestone was used. The 60-80-mesh calcite proved effective, but the corresponding-size dolomite was ineffective. Materials finer than 100-mesh were as effective as the hydrates, and the dolomitic stone was as good as the calcitic stone of this size.

The growth of alfalfa showed that the 20-40-mesh left in the soil was still ineffective. Both the calcitic and dolomitic 60-80-mesh separates, however, showed residual influence on the alfalfa.

¹ Contribution from the department of agronomy of the Pennsylvania State College. Paper No. 1688 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

The results of the soil analysis (table 2) 3 weeks after incorporation of the lime and fertilizer show that the coarse liming material was much less efficient than the fine material in correcting *all the conditions that* develop in too great degree in acid soils; namely, H-ion concentration, replaceable H, and replaceable Al, Mn, and Fe. Calcitic limestone performed these functions more rapidly than dolomitic stone of corresponding size. Apparently, it was necessary to raise this soil to a pH value of 5.3 to 5.4 to ensure germination and growth of crimson clover. This pH value was attained with 60-80-mesh calcitic stone, but 100-200-mesh dolomite was required to produce corresponding results in yield and in alteration of soil properties.

TABLE 1
Immediate and residual effect of calcitic and dolomitic separates on yields of legumes, experiment 1

POT NO.	LIMING MATERIAL, SCREEN	YIELD OF CRIMSON CLOVER PER POT	SOIL pH AFTER CLOVER	YIELD OF ALFALFA PER POT
		gm.		gm.
1	No lime	0	4.0	0
2	Calcitic stone 20-40	0	4.7	1.2
3	60-80	10.9	5.9	4.7
4	100-200	12.9	6.5	5.9
5	<200	15.1	6.5	6.5
10	Calcitic hydrate, <100	12.1	6.4	7.9
6	Dolomitic stone 20-40	0	4.6	0.1
7	60-80	1.4	5.2	6.3
8	100-200	12.7	5.8	7.1
9	<200	15.9	6.1	7.6
11	Dolomitic hydrate, <100	14.7	6.4	7.7

The pH values and the replaceable H, Al, Mn, and Fe in the soil after harvest of the crimson clover are shown in table 3.

The dolomitic and calcitic hydrates when used in equivalent amounts were equally effective, as shown in tables 1 and 3. This was true also for finely ground calcitic and dolomitic stones. Comparison of the coarse separates showed that the calcitic stone was more effective than the dolomitic material. For example, 60-80-mesh calcitic stone was about equal to 100-mesh dolomitic material in yield effects (table 1, fig. 1) and in correction of acidity (table 3).

These results prove that benefit of liming in this experiment was not due to addition of Ca as a nutrient, because all pots contained much more replaceable Ca than could possibly be required for the crop. Even the unlimed pot contained

800 pounds of replaceable Ca per 2,000,000 of soil. Part of this came from the superphosphate, because the original unlimed soil contained only 200 pounds.



FIG. 1. COMPARATIVE EFFICIENCIES OF CALCITIC AND DOLOMITIC LIMESTONE SEPARATES ON ACID SOIL

1, no lime; 2, 20-40-mesh calcitic; 3, 60-80-mesh calcitic; 4, 100-200-mesh calcitic; 5, 200 and finer mesh calcitic; 6, 20-40-mesh dolomite; 7, 60-80-mesh dolomite; 8, 100-200-mesh dolomite; 9, 200 and finer mesh dolomite.

Comparison of tables 1 and 3 shows that liming materials definitely decreased the replaceable Al and Mn and increased the replaceable PO_4 . The calcitic stone was more effective in performing these functions than was the dolomitic product.

TABLE 2

Analysis of Westmoreland soil sampled 3 weeks after treatment with calcitic and dolomitic separates, experiment 1

POT NO.	LINING MATERIAL, SCREEN	EXCHANGE- ABLE H ⁺	pH	REPLACEABLE ELEMENTS†						
				Al	Mn	Fe	Ca	Mg	K	P _i
		me.		lb.	lb.	lb.	lb.	lb.	lb.	lb.
1	No lime	8.7	4.1	140	50	50	800	190	200	2.5
2	Calcitic stone									
	20-40	6.5	4.5	90	20	0	1600	185	175	2.5
3	60-80	3.7	5.4	28	0	0	2200	180	175	2.8
4	100-200	3.1	6.0	15	0	0	2700	160	150	3.0
5	<200	3.1	6.1	13	0	0	3300	145	125	3.5
10	Calcitic hydrate, <100	2.8	6.1	12	0	0	2600	180	125	2.9
6	Dolomitic stone									
	20-40	7.7	4.4	95	25	10	1200	370	200	2.3
7	60-80	6.5	4.7	45	15	tr.	1100	600	200	2.3
8	100-200	5.3	5.3	31	0	0	1100	740	175	2.5
9	<200	4.1	5.8	15	0	0	1300	1000	175	2.6
11	Dolomitic hydrate, <100	3.1	6.1	13	0	0	1500	1000	175	2.6

* Per 100 gm.

† Per 2,000,000 pounds.

TABLE 3

Analysis of soil after harvest of crimson clover, 6 months after treatment with calcitic and dolomitic separates, experiment 1

	LINING MATERIAL, SCREEN	EXCH. H ⁺	pH	REPLACEABLE ELEMENTS†		
				Al	Mn	Fe
		me.		lb.	lb.	lb.
1	No lime	7.1	4.04	140	90	tr.
2	Calcitic stone					
	20-40	4.1	4.66	55	10	0
3	60-80	2.1	6.23	10	0	0
4	100-200	1.4	6.40	6	0	0
5	<200	1.6	6.54	6	0	0
10	Calcitic hydrate, <100	1.7	6.4	6	0	0
6	Dolomitic stone					
	20-40	5.8	4.62	65	15	tr.
7	60-80	4.4	5.04	22	tr.	0
8	100-200	2.8	6.04	9	0	0
9	<200	2.3	6.53	6	0	0
11	Dolomitic hydrate, <100	1.8	6.49	6	0	0

* Per 100 gm.

† Per 2,000,000 pounds.

TABLE 4

Influence of percentage lime requirement satisfied on soil analysis 3 weeks after treatment and on yields of crimson clover and alfalfa, experiment 2

POT NO.	LIMING MATERIAL*	LIME REQUIREMENT SATISFIED	pH	EXCH. H†	REPLACEABLE ELEMENTS‡							YIELD OF CLOVER PER POT	SOIL pH AFTER CLOVER	YIELD OF ALFALFA PER POT
					Al	Mn	Fe	Ca	Mg	K	PO ₄			
		%		mc.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	gm.		gm.
1	None	0	4.0	8.7	140	50	50	600	190	200	2.5	0	4.0	0
12	Cal. H	50	5.1	5.8	37	10	tr.	1500	165	130	2.5	5.56	5.2	3.10
13	Dol. H	50	5.2	5.4	37	tr.	tr.	1100	840	175	2.0	7.12	5.3	3.10
10	Cal. H	100	6.1	2.8	12	0	0	2600	180	125	2.9	12.34	6.4	7.93
11	Dol. H	100	6.1	3.1	13	0	0	1500	1000+	150	3.0	14.75	6.5	7.73
14	Cal. H	200	6.2	0.8	6	0	0	4500	120	100	6.0	10.34	7.4	7.57
15	Dol. H	200	7.0	1.1	8	0	0	2100	1000	115	6.0	12.52	7.5	7.67
16	Cal. H	400	7.4	0.0	4	0	0	8000	110	250	3.7	7.23	7.7	7.00
17	Dol. H	400	7.5	0.0	4	0	0	3200	1000+	200	4.8	5.81	7.9	7.50
18	Cal. S	50	5.2	5.5	37	7	tr.	1400	140	175	tr.	4.63	5.4	3.20
19	Dol. S	50	5.0	5.1	37	10	0	1000	760	125	1.0	5.31	5.2	1.03
4	Cal. S	100	6.0	3.1	15	0	0	2700	100	150	3.0	12.92	6.5	5.93
8	Dol. S	100	5.3	3.1	31	0	0	1100	740	175	2.5	12.67	5.8	7.13
20	Cal. S	200	6.7	1.1	6	0	0	5000	110	125	2.5	11.75	7.25	7.93
21	Dol. S	200	6.3	3.1	10	0	0	1500	1000+	125	2.5	14.88	6.9	7.15
22	Cal. S	400	7.4	0.0	3	0	0	7000	105	120	5.9	8.79	7.5	7.40
23	Dol. S	400	7.3	0.0	4	0	0	2500	1000	195	5.2	13.08	6.9	7.83

* Cal. H, Dol. H and Cal. S., Dol. S—refer to calcite and dolomitic hydrates and to stones 100-mesh and finer.

† Per 100 gm.

‡ Per 2,000,000 pounds.

TABLE 5

Effectiveness of large applications of coarse limestone or dolomite on yield of crimson clover and soil analysis at close of experiment 3

POT NO.	LIMING MATERIAL*	LIME REQUIREMENT SATISFIED	YIELD OF CLOVER PER POT	SOIL ANALYSIS AT CLOSE			
				pH	PO ₄	Al	Mn
		%	gm.		lb.	lb.	lb.
1		0	3.5	3.8	2.0†	45†	52†
11	Cal. S	300	41.0	4.9	1.0	35	30
12	Dol. S	300	29.3	4.5	1.0	52	35
13	Cal. S	600	45.1	5.1	4.0	22	22
14	Dol. S	600	32.4	4.7	1.0	32	40
15	Cal. S	900	47.5	5.3	5.5	20	22
16	Dol. S	900	42.9	5.0	3.0	27	32
17	Cal. S	1200	71.9	5.6	3.5	17	17
18	Dol. S	1200	64.3	5.2	3.0	20	25
3	Cal. S	100	72.5	6.8	5.0	4	3
4	Dol. S	100	65.0	6.5	3.5	5	6

* 10-20-mesh calcitic and dolomitic stone applied to all pots except unlimed No. 1 and check treatments, Nos. 3 and 4, which received 100-mesh and finer limestone and dolomite.

† Per 2,000,000 pounds.

EXPERIMENT 2—INFLUENCE OF PERCENTAGE OF LIME REQUIREMENT SATISFIED

In this experiment, the lime requirement was 0, 50, 100, 200, and 400 per cent satisfied with 100-mesh and finer calcitic and dolomitic hydrates and carbonates.

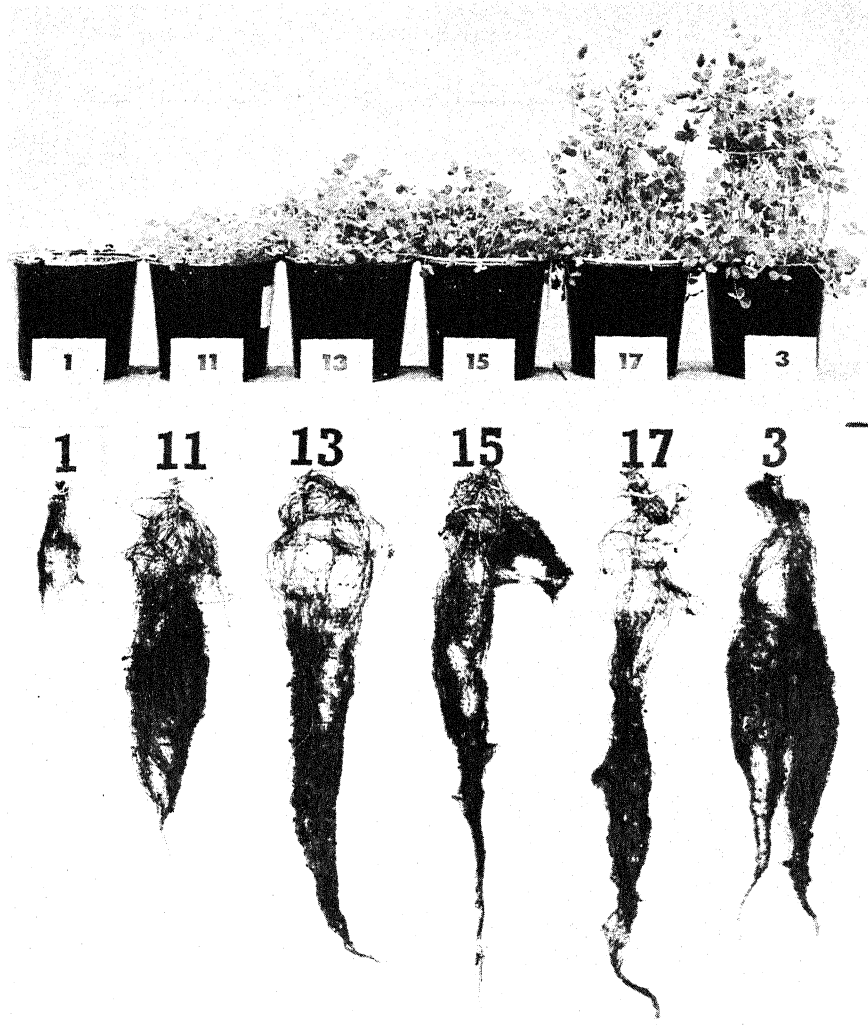


FIG. 2. EFFECTIVENESS OF HEAVY APPLICATIONS OF COARSE CALCITE ON YIELDS AND ROOT DEVELOPMENT OF CRIMSON CLOVER

1, no lime; 11, 300 per cent requirement satisfied with 10-20-mesh; 13, 600 per cent satisfied with 10-20-mesh; 15, 900 per cent satisfied with 10-20-mesh; 17, 1200 per cent satisfied with 10-20-mesh; 3, 100 per cent satisfied with 100-mesh.

Again, as in experiment 1, alfalfa was grown after crimson clover without additional lime but with a second application of fertilizer. Soil analyses were made and crop yields determined as in experiment 1.

Table 4 shows that when the lime requirement was 100 per cent satisfied, the yields were as good as when the requirement was 200 or 400 per cent satisfied. When the requirement was 400 per cent satisfied with hydrates, pH values of

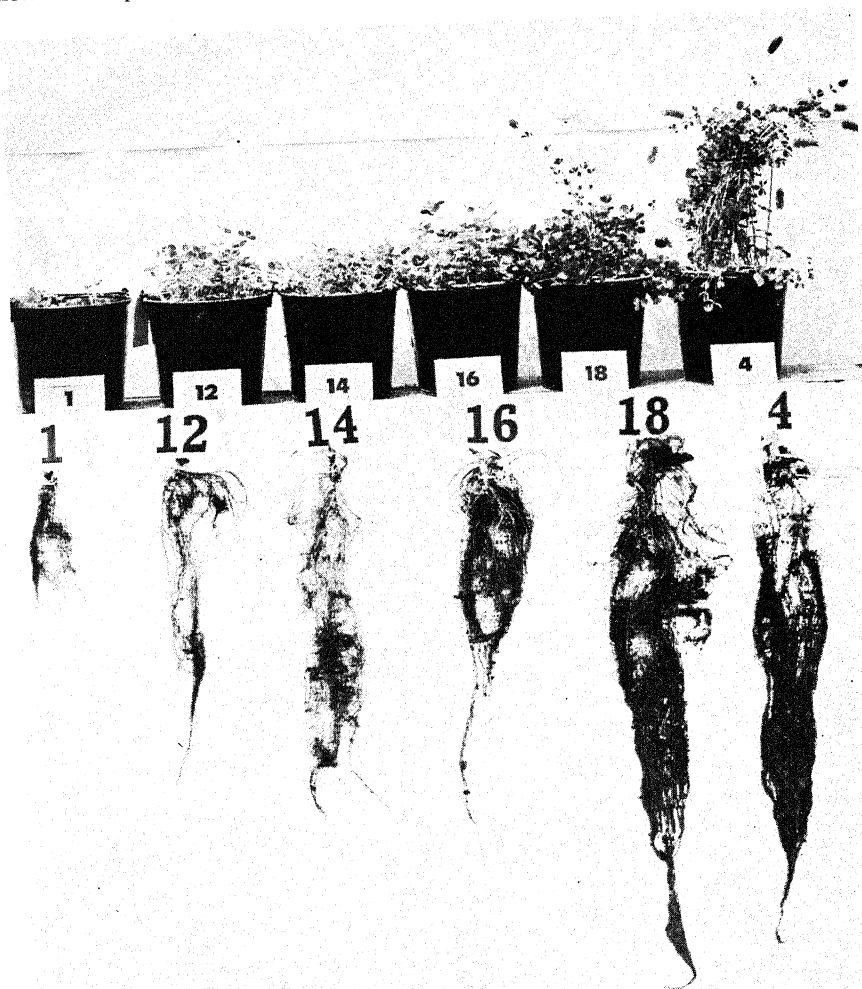


FIG. 3. EFFECTIVENESS OF HEAVY APPLICATIONS OF COARSE DOLOMITE ON YIELDS AND ROOT DEVELOPMENT OF CRIMSON CLOVER

1, no lime; 12, 300 per cent requirement satisfied with 10-20-mesh; 14, 600 per cent satisfied with 10-20-mesh; 16, 900 per cent satisfied with 10-20-mesh; 18, 1200 per cent satisfied with 10-20-mesh; 4, 100 per cent satisfied with 100-mesh.

7.4 and 7.5 were obtained and the yields were lowered thereby. On this soil, satisfying 50 per cent of the lime requirement failed to inactivate the Al and Mn. Replaceable PO_4 was increased by increasing amounts of hydrate and carbonate until a pH of about 7.4 was reached, then it was lowered slightly.

Soil analyses after harvest of the clover, not given in table 4, showed that

replaceable Fe was absent in all cases, there were only traces of Mn, and Al was reduced to a few pounds in all except the pots limed to 50 per cent of the requirement and the check pot.

EXPERIMENT 3—EFFECTIVENESS OF HEAVY APPLICATIONS OF COARSE LIMESTONE

Conceivably, if coarse limestone could be purchased cheaply enough, it would be possible to make such heavy applications that plant root tips would always be in contact with particles of limestone. To investigate this possibility, 10–20-mesh calcitic and dolomitic limestones were applied in amounts equivalent to 300, 600, 900, and 1200 per cent of the lime requirement of the soil. As a check treatment, 100-mesh limestone equivalent to the lime requirement was used. The yields of crimson clover and the analyses of the soils sampled at the close of the experiment are presented in table 5, and in figures 2 and 3.

Table 5 brings out several points.

First, the coarse material is quite inadequate in raising the pH value, lowering the active Al and Mn, and increasing the availability of PO_4 . It is also inadequate in increasing yields. Very heavy applications, however, tend gradually to catch up to the 100-mesh material. The heaviest application of coarse material represented 45.6 tons of CaCO_3 per acre. Obviously, the cost of transporting such a large amount would absorb the profits from its use.

Second, the dolomitic stone was less effective than the calcitic stone in increasing yields, in raising the pH and available PO_4 , and in reducing the active Al and Mn. All of the soils contained considerable replaceable Ca at the close of the experiment, in fact, none contained less than 500 pounds per acre. Available Ca as a nutrient, therefore, could not have been limiting in any case. This together with much other evidence, indicates strongly that the function of liming is to reduce the toxicity of Al and Mn and raise the availability of PO_4 .

CONCLUSIONS

Calcitic and dolomitic hydrates used in chemically equivalent amounts were equally effective in raising pH values, lowering replaceable H, Al, and Mn, and promoting growth of crimson clover.

Calcitic and dolomitic limestones 100-mesh and finer are virtually equal to the corresponding hydrates in increasing yields and in raising pH values and lowering the replaceable H, Al, and Mn.

Coarse dolomitic limestone is much less soluble in acids than is calcitic stone of equal size, and it is less effective in promoting germination and the growth of tops and roots of crimson clover. It is likewise less efficient in raising the pH and lowering the replaceable H, Al, and Mn.

Where large quantities of coarse (10–20-mesh) calcitic and dolomitic limestones were mixed into very acid soil the influence in promoting top and root growth of crimson clover was closely related to the elevation of pH and the lowering of replaceable H, Al, and Mn by the treatments.

Merely satisfying the lime requirement was as effective in promoting growth as were applications twice and four times the lime requirement.

SOIL SCIENCE

VOLUME 73

February 1952

NUMBER 2

A NONSTATIONARY METHOD FOR DETERMINING THERMAL CONDUCTIVITY OF SOIL IN SITU

D. A. DE VRIES¹

Landbouwhogeschool, Wageningen, Holland

Received for publication June 22, 1951

An accurate determination of the thermal conductivity of soils *in situ* is important in soil physics, meteorology, and agricultural and civil engineering. The only method that could be found in literature is the one developed by Albrecht (1) and applied by Franssila (4) and Bracht (2). This method is based on the theory of steady flow of heat.

Because the transport of heat in a moist porous material is accompanied by distillation of water vapor, the author has argued elsewhere (7) that a non-stationary method and the use of small temperature gradients are preferable in measuring the thermal conductivities of soils. Such a method has been developed by Van der Held and Van Drunen (5) for determining the thermal conductivity of liquids. Earlier work on this method was that of Stålhane and Pyk (6) and of Weishaupt (8). The method has already been applied by Van Dorsen (3) to the measurement of thermal conductivity of sand at low moisture contents in the laboratory.

This article discusses the construction of a cylindrical element that can be placed in the soil to measure its thermal conductivity by the aforementioned method and presents some of the results obtained. An important feature is the small diameter of the cylinders, which makes it possible to introduce them into the soil without markedly disturbing the natural structure.

PRINCIPLE OF THE METHOD

The thermal conductivity of the material under investigation is measured by introducing a long electrically heated wire in the (homogeneous) material, switching on the heating current in this wire, and measuring the rise of temperature with a thermocouple somewhere near the middle of the wire.

For a linear heat-source of infinite length, the rise of temperature (θ) at radial distance r from the source is represented by:

$$\theta = (q/4\pi\lambda) \{ -Ei(-r^2/4at) \} \quad (1)$$

¹ The author is indebted to W. R. van Wijk for his interest in this work and for useful suggestions, to E. M. F. van der Held for his kindness in showing the thermal conductivity measurements in progress at his laboratory, and to L. Admiraal for his help with the construction of the elements and the carrying out of the measurements.

where q = the amount of heat produced per unit time and unit length of the source, λ = the thermal conductivity of the material, a = the thermal diffusivity of the material, t = time,

$$-Ei(-\kappa) = \int_{\kappa}^{\infty} (1/\kappa) \exp(-\kappa) d\kappa = -0.5772 - \ln \kappa + \frac{\kappa}{1 \cdot 1!} - \frac{\kappa^2}{2 \cdot 2!} + \dots$$

Thus for small values of $r^2/4at$:

$$\theta = (q/4\pi\lambda) \{c + \ln t\}, \quad (2)$$

where c is independent of time.

By plotting the rise of temperature against $\log t$, we obtain a straight line. λ can be calculated from the slope of this line, if the heating current and the resistance per unit length of the heating wire are known.

Van der Held and Van Drunen (5) have shown that the corrections, which are caused by the finite radius of the heat source and the deviations of the Ei -function from the logarithmic function, can be taken into account by introducing in (2) a time correction t_0 . Now with good approximation:

$$\theta = (q/4\pi\lambda) \{d + \ln(t + t_0)\}$$

where d is again independent of time. They also showed how t_0 can be evaluated from the experimental data by an easy graphic method. The influence of the finite length of the heating wire can be made arbitrarily small by extending its axial dimension.

When the heating current is switched off, the temperature falls again. Now the thermal conductivity can also be measured by determining the fall of temperature as a function of time. Switching off the current at time t_1 is equivalent to introducing at that time a heat sink which removes heat at a rate q per unit time and length. For a linear source we now find:

$$\theta = (q/4\pi\lambda) \{-Ei(-r^2/4at)\} \quad \text{for } t \leq t_1, \quad \text{and}$$

$$\theta = (q/4\pi\lambda) \{-Ei(-r^2/4at)\} - (q/4\pi\lambda) \{-Ei(-r^2/4a(t - t_1))\} \quad \text{for } t \geq t_1,$$

which becomes for small values of $r^2/4a(t - t_1)$:

$$\theta = (q/4\pi\lambda) \ln t/(t - t_1) \quad \text{for } t - t_1 > \tau,$$

where τ depends on r and a .

Similarly we find for a source with finite radius:

$$\theta = (q/4\pi\lambda) \{d + \ln(t + t_0)\} \quad \text{for } \tau^1 < t \leq t_1, \quad \text{and}$$

$$\theta = (q/4\pi\lambda) \{d + \ln(t + t_0)\} - (q/4\pi\lambda) \{d + \ln(t - t_1 + t_0)\} \quad \text{for } t - t_1 > \tau^1$$

The value of $(q/4\pi\lambda) \{d + \ln(t + t_0)\} - \theta$ in the last expression plotted against $\log(t - t_1 + t_0)$ must again give a straight line with slope $q/4\pi\lambda$. The required value of $(q/4\pi\lambda) \{d + \ln(t + t_0)\}$ can be readily found by extrapolating the line obtained for $t \leq t_1$.

CONSTRUCTION OF THE MEASURING ELEMENT

In the soil the heating wire and the thermocouple wires must be adequately protected. In our first elements they were placed in a glass capillary filled with paraffine oil. Although good results could be obtained in this way, the glass elements proved to be too fragile.

The construction of the elements now in use is illustrated in figure 1. The heating wire is enameled constantan of 0.01 cm. diameter. It is folded and introduced into a glass capillary with an outside diameter of about 0.04 cm. The outer cover is of fine monel gauze. This gauze is rolled along a metal wire so that it forms a socket of about 0.14 cm. outer diameter. Because the individual wires of the gauze interlock closely at the seam, no soldering is necessary.

The thermocouple wires are of enameled copper and constantan, 0.01 cm. in diameter. The junction is covered with a thin layer of collodion to provide a good electrical insulation from the gauze. The thermocouple wires and the glass capillary are introduced into the gauze cylinder, and after this the space

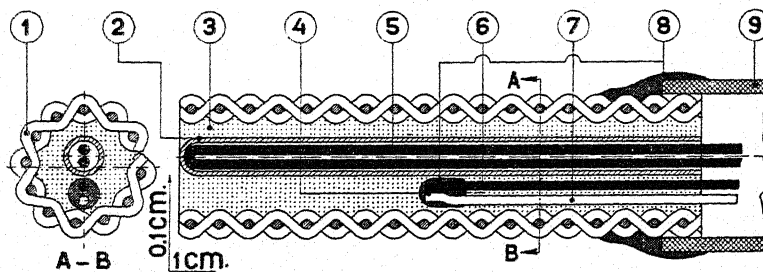


FIG. 1. RADIAL AND LONGITUDINAL CROSS SECTION THROUGH A MEASURING ELEMENT

1—monel gauze; 2—glass capillary; 3—paraffine wax; 4—thermojunction; 5—heating wire; 6—constantan; 7—copper; 8—collodion; 9—insulating socket.

between the glass and the gauze is filled with molten paraffine wax, which becomes hard after cooling.

The advantages of this construction are as follows:

1. The gauze cover and the paraffine wax give the element sufficient rigidity.
2. The metal of the gauze provides a good thermal contact between the element and the soil.
3. The glass capillary provides an excellent electrical insulation between the heating wire and the thermojunction.
4. The glass capillary allows some space between the heating wire and the thermojunction. If the junction lies next to the heating wire, the measured rise of temperature is very fast in the beginning, whereas the rate of rise is determined largely by the thermal properties of the paraffine wax.

With these elements the observed values of t_0 have been less than 2 seconds; in most cases, less than 1 second. The length of the element is about 10 cm.

Both ends of the heating wire are soldered to copper wires of 0.3 cm. diameter. The cold junction of the thermocouple can be placed in the soil at the same height as the warm junction, or in a thermos flask filled with melting ice above

the soil. The wires extending from the element are protected by a socket of plastic insulating material.

MEASURING THE THERMAL CONDUCTIVITY

After a small trench is dug to the required depth, a horizontal hole is bored in the side with a metal wire 0.1 cm. in diameter. An element is introduced into undisturbed soil through the hole to guard the element against damage from contact with stones or other hard materials. The trench is then filled. Thus, disturbance of the soil in the neighborhood of the measuring thermojunction is very slight. The wires are connected to a cable, which leads to the instruments inside the laboratory.

The rise of temperature is measured with a sensitive micro-Moll galvanometer, with a period (undamped) of 0.2 second. The time is read on a stopwatch, when the center of the light-spot passes a division on a millimeter scale. The maximum rise of temperature at the warm junction is about $1.5^{\circ}\text{C}.$, which corresponds with a deflection of about 3 cm. on the scale in our experiments. Corrections due to the inertia of the galvanometer are negligible about 5 seconds after the start of an experiment.

Resistances are measured with a sensitive D.C. Wheatstone bridge. The resistance of the heating wire is $0.631 \Omega/\text{cm}.$

The heating current, which is about 0.1 ampere, is supplied by a 6-volt storage battery. The heating is carried on for about 3 minutes.

The first reliable point is usually obtained after about 10 seconds. For $t < 5$ seconds the influence of the finite thickness of the element, the inertia of the galvanometer, and the deviations of the Ei -function from the logarithm are relatively large. The correction t_0 , which is of importance only for $t < 60$ seconds, can be neglected in many cases, or its value can be read directly from the graph of the galvanometer deflection against $\log t$ by drawing a straight line through the points with $t > 60$ seconds (cf. fig. 2, curve b).

With the cold junction in the soil at the same height as the warm junction, changes in deflection of the galvanometer due to temperature changes in the soil are usually negligible. Care must, of course, be taken that sufficient space exists between the cold junction and the wires, which carry the heating current. With the cold junction in ice, the readings must be corrected for these temperature changes, since they cause a lapse of the light-spot on the scale at zero heating current. Small movements of the light-spot in one direction, which have not been taken into account, are reflected by a small difference in slope between the heating and the cooling line (cf. fig. 2, curve a).

RESULTS

Some of the measured logarithmic lines are represented in figure 2.

Some results obtained with four elements at depths of 4, 8, 16, and 32 cm. in clayey soil cropped with short cut grass are collected in table 1, which also contains rainfall measurements. The four elements are placed approximately in the same vertical plane. A more detailed presentation of results for May 4-5 is

shown in figure 3, together with recordings of rainfall and of the temperatures of the thermocouples in the elements (on a Brown Elektronik recording potentiometer).

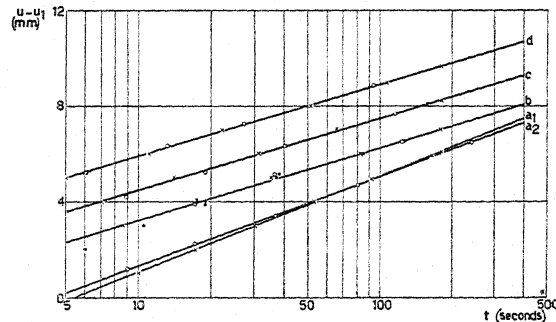


FIG. 2. GALVANOMETER DEFLECTION AGAINST LOG t

For the lines obtained on cooling, t means the time that elapsed after the heating current was switched off. To avoid overlapping of curves, the actual deflections (u) were diminished by an amount u_1 , which was taken different for different curves. \times = heating, \circ = cooling, \cdot = not corrected for t_0 . a_1 , May 3, depth 8 cm., t_0 = heating; a_2 , May 3, depth 8 cm., t_0 = 0, cooling; b , May 4, depth 16 cm., t_0 = -1.9; c , May 9, depth 4 cm., t_0 = 0; d , May 9, depth 32 cm., t_0 = 0.

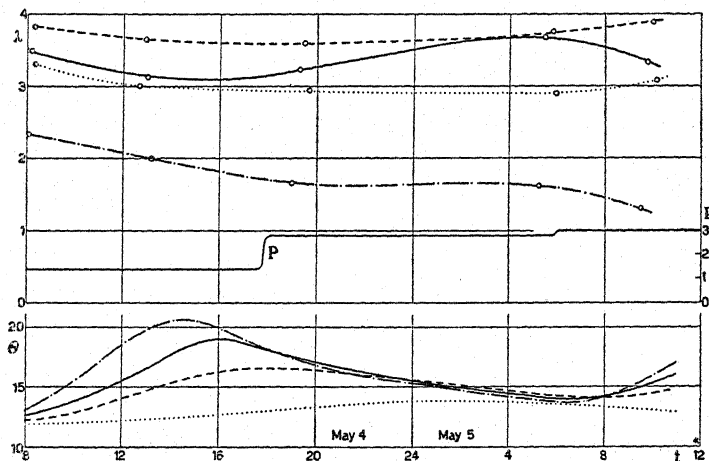


FIG. 3. THERMAL CONDUCTIVITY λ (IN MILLICALORIES/CM./SECOND/°C.), TEMPERATURE θ (IN °C.) AND PRECIPITATION P (IN MM.) AGAINST TIME t (IN HOURS LOCAL MEAN TIME)

— · — · — depth 4 cm.; — depth 8 cm.; - - - - - depth 16 cm.;
..... depth 32 cm.

The accuracy of the measurements is mainly governed by the accuracy with which the slope of the lines can be determined. In general the over-all accuracy is about 3 per cent. In the dry top layer at 4 cm. depth of the clayey soil on May 4-5, however, the accuracy was less, because the slopes of the heating and

the cooling lines differed by as much as 10 to 20 per cent.² Probably this was due to inhomogeneity of the soil (for example, a steep moisture gradient); this point is still under investigation.

From the results it follows that daily trends in the moisture contents at several depths and the seepage of rain into the soil can be deduced from the thermal conductivity measurements.

TABLE 1
Values of the thermal conductivity* at various depths of clayey soil cropped with grass†

DATE	TIME (h)	λ_1	λ_2	λ_8	λ_{32}	P‡
May 1	13	3.30	3.60	3.76	3.72	0.0
May 2	8	3.20	3.52	3.87	3.30	0.0
	13	3.24	3.73	3.55	3.16	
May 3	14	2.88	3.59	3.60	3.29	1.4
May 4	8	2.32	3.48	3.82	3.38	0.0
	13	1.97	3.12	3.66	3.02	
	19	1.74	3.22	3.60	2.93	
May 5	6	1.57	3.70	3.74	2.88	1.6
	10	1.29	3.34	3.89	3.08	
May 6	—	—	—	—	—	3.1
May 7	9	2.92	3.50	3.94	3.00	7.2
	15	2.78	3.52	3.44	2.68	
May 8	9	4.52	3.39	3.72	3.60	14.4
	14	4.44	3.70	3.94	3.50	
May 9	8	4.55	3.78	4.50	3.78	0.8
May 10	8	4.16	3.64	4.10	3.10	0.0

* In millicalories per centimeter per second per degree C.

† $\lambda_1, \lambda_2, \lambda_8, \lambda_{32}$, refer to depths of 4, 8, 16, and 32 cm.

‡ P = rainfall, in millimeters per day, measured at 8 a.m. local mean time.

SUMMARY

The construction of a cylindrical measuring element of small dimensions (length about 10 cm., diameter about 0.14 cm.) for measuring the thermal conductivity of soil *in situ* is described. The method is based on the theory of nonstationary flow of heat from a long cylindrical source with small radius, as developed by Van der Held and Van Drunen.

The elements are placed horizontally in the soil. Because of their small radius, the disturbance of the soil near the element is only slight. Another advantage of the method is its rapidity; moisture transport during the measurement is therefore negligible.

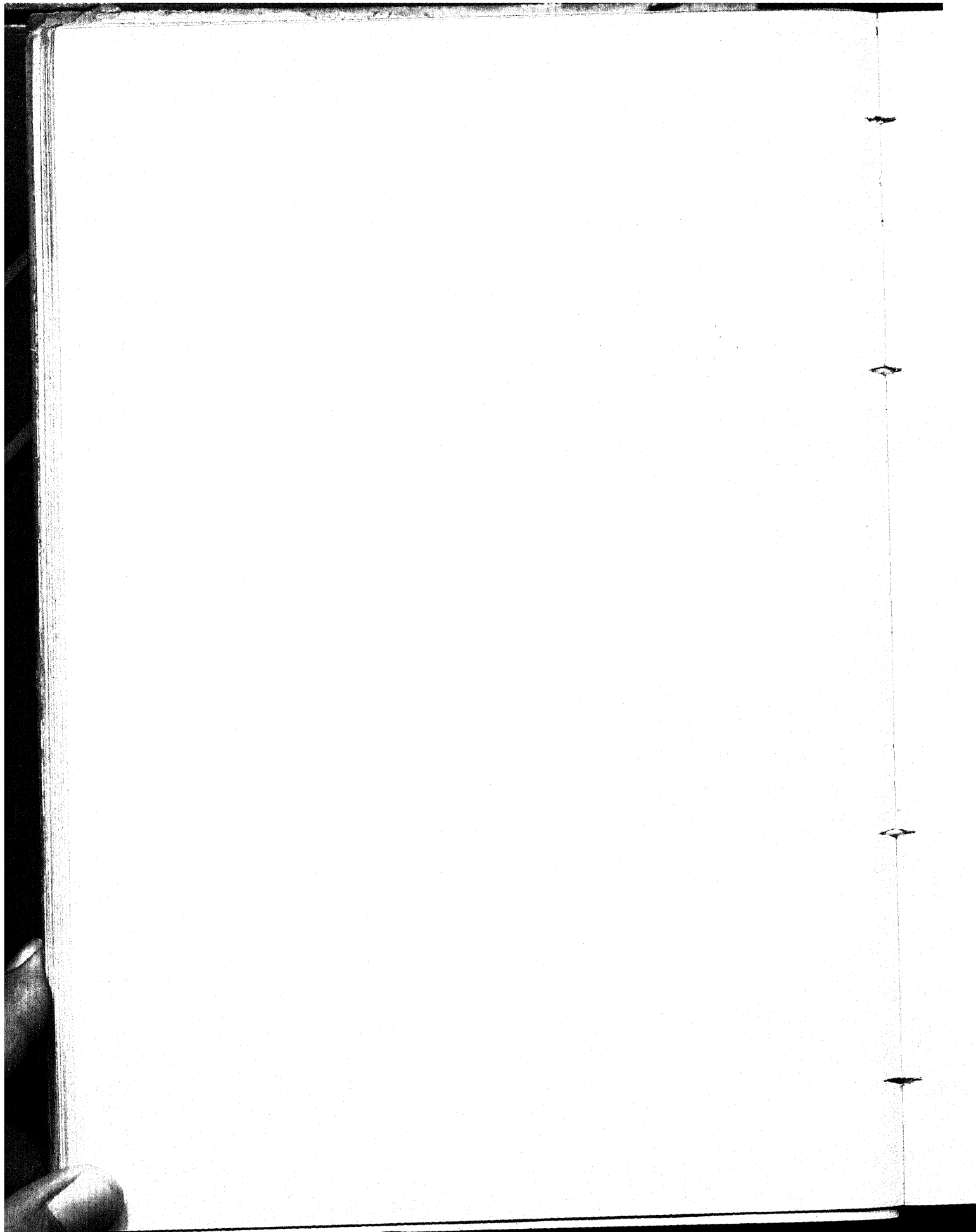
Some results obtained by the method are presented. Daily trends in moisture content and the seepage of rain into the soil are reflected in the measured values of the thermal conductivity.

REFERENCES

- (1) ALBRECHT, F. 1932 Ein Messgerät für die Messung des Wärmeumsatzes im Erdboden. *Met. Ztschr.* 49: 294-299.

² In all cases the arithmetic mean of the slopes of the heating and the cooling line was taken to calculate λ .

- (2) BRACHT, J. 1949 Über die Wärmeleitfähigkeit des Erdbodens und des Schnees und den Wärmeumsatz im Erdboden. *Veröffentl. Geophys. Inst. Univ. Leipzig* (ser. 2) 14: 3.
- (3) DORSSSEN, J. C. VAN 1949 Nijverheidsorganisatie Toegepast Natuurwetenschappelijk Onderzoek. Rap. 7.
- (4) FRANSILA, M. 1936 Mikroklimatologische Untersuchungen des Wärmehaushalts. Mitt. Met. Zentralanstalt Helsinki 20.
- (5) HELD, E. M. F. VAN DER, AND DRUNEN, F. G. VAN 1949 A method of measuring the thermal conductivity of liquids. *Physica* 15: 865-881.
- (6) STÅLHANE AND PYK 1931 Teknisk Tidskrift.
- (7) VRIES, D. A. DE 1950 Some remarks on heat transfer by vapour movement in soils. *Trans. 4th Internat. Cong. Soil Sci.* 2: 38-41.
- (8) WEISHAUPT, J. 1940 Nicht stationäres Verfahren zur Bestimmung der Wärmeleitzahl von Flüssigkeiten. *Forschung* 11: 20-35.



GASEOUS DIFFUSION AND POROSITY IN POROUS MEDIA

C. H. M. VAN BAVEL

North Carolina Agricultural Experiment Station¹

Received for publication May 23, 1951

From the beginning of research in soil physics it has been apparent that some relationship should exist between the rate at which gases diffuse through soil and its porosity, that is, the volume fraction occupied by the gaseous phase. Various investigators have sought with fair success to establish a law predicting the diffusion rate from the porosity. This situation is entirely different from the status of the query for a relation between porosity and permeability, a search which Childs and George (2) have recently shown to be futile.

If one sides with the present opinion that diffusion is the predominant process governing soil aeration, the importance of a relation between rate of diffusion and porosity is clear. It is difficult to suggest a good method for measuring the rate of diffusion of undisturbed soil in the field, though Raney (12) recently reported an attempted procedure. On the other hand, prevailing porosity can be readily determined in the field, and Russell (13) has proposed equipment for this purpose. From the porosity one might then calculate the diffusion rate and use this figure, in turn, as a soil characteristic. The diffusion rate for a particular gas forms an integral part of a complete description of the soil aeration process, as the author (16) recently attempted to demonstrate.

This paper reports the results of a reexamination of this relationship. Utilization of a precise experimental technique and analysis of the data with the result of an exhaustive theoretical treatment are believed to give a satisfactory degree of reliability to these results.

LIST OF SYMBOLS

Throughout this paper the following symbols and units are used:

- A = area in cm^2 .
- D = diffusivity of a gas through air in a porous medium in cm^2/sec . as defined by $\delta p/\delta t = D\nabla^2 p$
- D_0 = diffusivity of a gas through open air in cm^2/sec .
- P = total pressure in mm. Hg
- P_A = barometric pressure in mm. Hg
- p = partial pressure in mm. Hg
- p_a = partial pressure of air in mm. Hg
- p_v = partial pressure of vapor in mm. Hg
- p_{vp} = vapor pressure (saturated) in mm. Hg
- c_a = concentration of air in gm./cc.
- c_v = concentration of vapor in gm./cc.

¹ Contribution from the agronomy department of the North Carolina Agricultural Experiment Station, Raleigh. Paper No. 387 of the Journal Series. The author wishes to acknowledge the help of Mrs. H. F. Krackenberger, who made most of the measurements and computations.

- q = quantity of gas, or vapor, in gm.
 u = velocity of mass flow of gas in cc./second
 k = permeability of porous medium in darcy
 μ = viscosity of gas in centipoise
 t = time in seconds
 T = absolute temperature in °K
 Q_v = vapor flux in gm./cm.²/second
 R_v = gas constant of vapor in mm. Hg. cc./°K/g
 (In this definition the cc. are meant as cc. of the porous medium, which makes R_v inversely proportional to the porosity, other conditions being equal. This definition deviates from the customary one, but is adapted to the terminology used in soil aeration work.)
 β = $R_v T$ in mm. Hg cc./gm.
 x, y = coordinates in real or complex plane in cm.
 $i = \sqrt{-1}$
 $z = x + iy$ = complex variable
 u, v = coordinates in complex plane
 $w = u + iv$ = complex variable
 r, e = polar coordinates in cm. and radians respectively
 In addition, some constants like a, b , and w will be used.

PREVIOUS INVESTIGATIONS

Previous investigations of the relation between diffusion and porosity have, in essence, involved maintaining a constant difference in partial pressure of a gas or vapor between the two end-faces of a column of some porous material, usually sand or soil. Then, in some way, the rate of gas or vapor transfer was measured.

Buckingham (1) passed a stream of CO₂ and CO₂-free air over the two ends of a soil column contained between wire mesh and analyzed the air after it had picked up CO₂ that had diffused through the soil column. He recognized the danger of setting up total pressure differences and tried to avoid these with an intricate counterbalancing valve system and to observe any pressure differences with a sensitive manometer. The effect of the wire mesh was neglected in these measurements. Buckingham claimed that his manometer would indicate pressure differences as small as 2×10^{-3} mm. Hg. In a typical experiment (1, p. 16) a rate of transfer of CO₂ was observed of 7×10^{-4} cc./second/cm². This took place through a column 5 cm. long. If one supposes that a total pressure difference of 1×10^{-3} mm. Hg was operative, but unobserved, and if the permeability of the soil is taken as 10 darcys [compare Muskat (7, p. 113)], the rate of transfer due to the total pressure difference can be calculated by Kirkham's formula (6, p. 96):

$$\frac{dq}{dt} = \frac{k}{\mu} \frac{\Delta P/760}{\text{length of column}}$$

When μ is taken as 1.8×10^{-2} centipoise², dq/dt is equal to 1.4×10^{-4} cc./second/cm.² From comparison it appears, therefore, that even with the careful experimentation of Buckingham, serious errors may occur. By making several observations, a satisfactory average value may nevertheless be obtained, but

² Handbook of Physics and Chemistry, viscosity of air.

it would be preferable to use a method in which no total pressure differences can be incurred.

Smith and Brown (14) used a technique not unlike Buckingham's but employing ordinary water manometers to ascertain equality of pressure. The results obtained were erratic, and these workers expressed doubts as to the validity of Buckingham's results.

Hagan (4) made an elaborate investigation also employing a "sweep" technique, using CS_2 vapors. In these experiments no arrangement was provided to check whether the pressure on each side of the column was equal. From the description of the apparatus it is clear that only very small pressure differences might have occurred, but on the other hand, it has been shown that even the smallest differences have serious consequences for the dependability of the results. In the experiments of Hagan no evaluation was made of the resistive influence of the supporting screen. Hagan concludes as the result of his measurements at different temperatures that diffusion rate does not vary linearly with the pressure gradient. This is contradictory to all other work on diffusion in general, and as an explanation of the nonlinearity of the observations, the following is offered.

In the pertaining experiments, the CS_2 -air ratio in the mixture varied as much as 15:1 to 1:4. Although the diffusivity is known to be substantially independent of the concentration ratio over a wide range, one could not expect such to be the case for the wide variation that prevailed in the discussed experiment, that is, the diffusivity is not a constant in the equation.

Penman (10), conducted experiments with CO_2 using the sweeping air technique. These measurements are subject to similar criticism concerning the observation of any occurring total pressure differences. An attempt was made to evaluate the contribution to the total impedance made by the supporting grid or screen by means of a "blank" determination. In doing so, even with careful control of draft and temperature, one has no assurance as to complete absence of eddy currents in the air, and in our view the correction thus obtained is only approximate. Moreover, particles tend to lodge in a screen supporting sand or soil in such a fashion as to close it off rather effectively. Childs (2) mentioned the grid effect as a serious impediment in determining soil permeability values.

Total pressure differences of undetermined nature are excluded with an evaporation technique, as used by Penman (9) in another series of measurements, and one may regard this method as more precise than the ones discussed previously. In addition, the basis of the measurements is weighing, which can be carried out to a high degree of precision. The method used by Penman is nevertheless open to three criticisms. The first pertains to the evaluation of the grid effect, already discussed. The second—recognized in Penman's paper—concerns the variability of the diffusion constant due to different vapor-air ratios at different temperatures and at different points in the diffusion column. Furthermore, there is some uncertainty in the exact determination of the surface temperature of the evaporating liquid. The third objection is a matter of the appli-

cable theory, as explained in the following. Closure of the container on one side causes a current of air-vapor mixture to flow in the same direction as that of the vapor diffusion. This causes the partial pressures to vary exponentially rather than linearly, an effect that may not be neglected without serious error. This peculiar effect was known to the earliest students of diffusion, like Stefan and Winkelmann, as quoted by Pochettino (11). It was rigorously treated by Nusselt (8), whose derivations were substantially reproduced with clarifying comment by Jakob (5).

The latest contribution to the relation between porosity and diffusion rate was made by Taylor (15). His methodology is open to objections similar to those raised in the previous paragraph to Penman's experiment and theory.

The foregoing review is not meant to imply that the earlier results are of small value but merely to show that the methods used so far are open to improvement and that thus the important relationship under investigation might perhaps be ascertained with greater accuracy. In fact, with exception of the work of Smith and Brown (14), all experiments have yielded substantially similar results. The values obtained by Penman in the evaporation experiments can perhaps be taken as the most dependable. They show that: $D = 0.66D_0$. In comparing this latter expression with the one given in Penman's paper, one should have in mind that D in this paper is defined slightly differently, namely, as pertaining to the medium as a whole (and therefore equal to Penman's D/S , in which D refers to the gaseous phase and S is the porosity).

PROCEDURE

To obviate the influence on the measurements effected by a supporting screen or wire mesh, a semicircular container was designed. This tube (fig. 1) was made of thin (0.15 mm.) brass sheet and had a uniform cross-sectional area of $2.54 \times 2.54 \text{ cm}^2$. The inner radius was 2.54 cm. and the outer radius 5.08 cm. To one end a circular basin of approximately 2.5 cm. radius was so fastened that if the basin was filled with 5 ml. liquid, the liquid surface would not be farther than a few millimeters from the rim of the tube. The basin could be closed with a rubber lid, made from a No. 12 stopper, and the pliability of the brass sheet ensured a tight closure. Careful measurements with both ends closed proved that the tube was closed completely in this manner. A small resistance thermometer, previously calibrated, was attached to the underside of the rubber lid, and two prongs were carried through the lid so that a small plug could be inserted. The thermistor was placed so that it would be just immersed in the liquid. Thus the temperature of the liquid could be measured without opening the lid.

All experiments were conducted in a room in which the temperature fluctuated not more than 1°C . and the relative humidity between 50 and 70 per cent. A thermometer was placed in the balance case used, and a thermograph next to the balance to detect any temperature abnormalities.

After much experimentation ethyl alcohol was chosen as the evaporating liquid. Its vapor pressure is rather low (59.6 mm. Hg at 25°C .), which necessitates accurate weighing but which has the advantage that the alcohol-air

ratio of the mixture does not vary greatly and constancy of D_0 for alcohol into air may be assumed.

The tube of known volume was filled with air-dry sand or soil mixtures of varying porosity, the latter being determined after filling in the usual manner. The basin was filled with alcohol, the lid closed, and the assembly placed on the pan of an analytical balance with front and back doors removed. A tiny blower was directed so that a gentle air stream would flow over the open end of the tube, thus ensuring that the partial pressure of alcohol there was zero. After allowing sufficient time for reaching equilibrium, weighings were made every

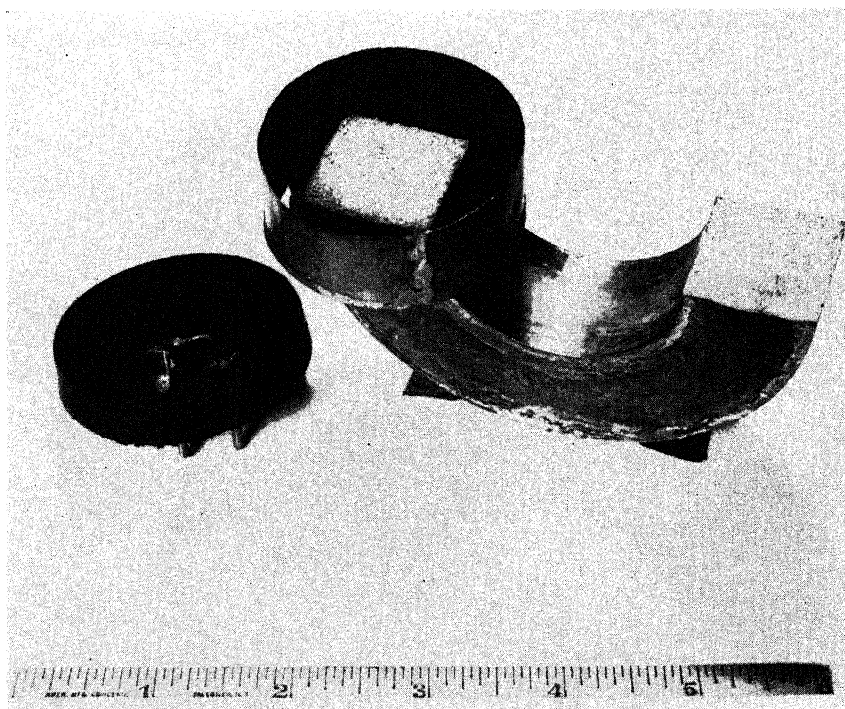


FIG. 1. SEMICIRCULAR DIFFUSION TUBE, FILLED WITH SAND

The bottom side of the lid shows the resistance thermometer.

half hour to the nearest 0.1 mgm. Temperature of the liquid to the nearest 0.1°C. and barometric pressure to the nearest 0.01 inch of Hg were also recorded with every weighing. The whole assembly is shown in figure 2.

The equilibrium time may be several hours, presumably because of some adsorption of alcohol on the material. This phenomenon was studied in more detail by Penman (9). A graph was made of the weight decrease *versus* time and a straight line was always obtained (fig. 5), from which the average dq/dt was calculated. The diffusivity D was then calculated from:

$$D = \frac{dq/dt \cdot 3.141 \cdot \beta}{0.693 \cdot 2.54 \cdot P_A \log [(P_A - p_{vp})/P_A]}$$

in which the values for β , P_A and p_{vp} are taken as the average ones for the duration of the experiment, usually 6 to 7 hours. Use of this formula is justified in detail in the next section.

In this formula no account is taken of the impedance of the path from the liquid surface to the closed end of the tube. From the calculations of Penman (9) for a similar situation and from the geometry of the path in our experiment, one may safely conclude that this influence is negligible.

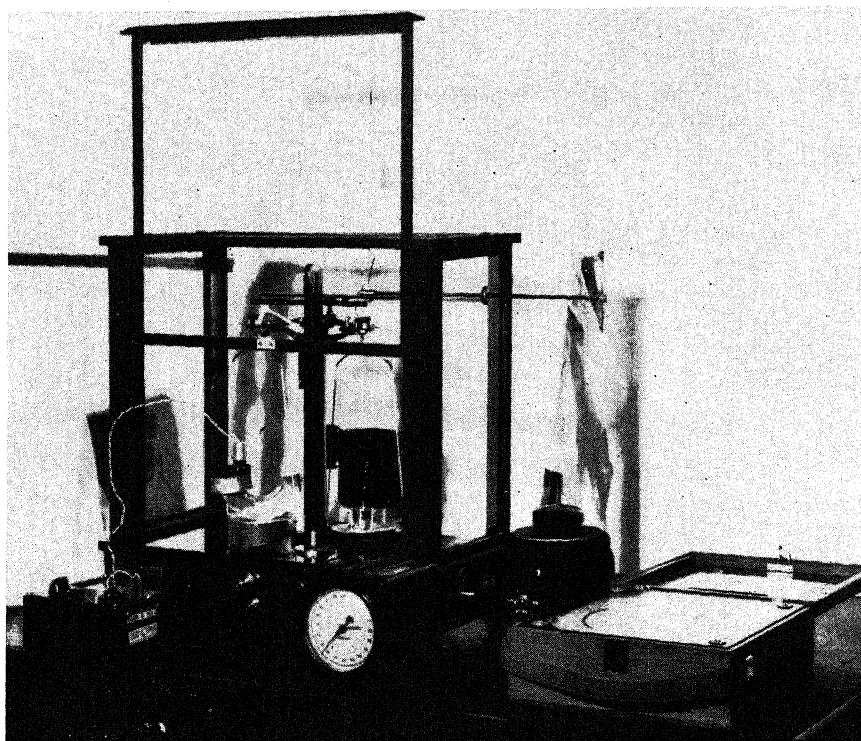


FIG. 2. THE EXPERIMENTAL ASSEMBLY

Behind the balance case is the blower. In front of the case are the ohmmeter and timer. To the right of the balance are the barometer and a variable transformer to regulate the blower. The evaporating tube with the lid closed and thermometer connected is on the left pan.

Since the fact that $D = (\text{constant}) \cdot D_0$ had been sufficiently established by Penman (9), and since the primary purpose of the present investigation was to obtain the value of the constant with greatest possible reliability, measurements were made at only three porosities.

THEORETICAL ANALYSIS

The distribution of partial pressures of a gas diffusing through a porous medium is given by

$$\frac{\delta p}{\delta t} = \nabla^2 p \quad (1)$$

or, when steady state only is considered, as will be done from now on,

$$\nabla^2 p = 0 \quad (2)$$

For a straight tubular region of the medium with impermeable walls, length d , and partial pressures p_1 and p_2 at the end faces, p follows from

$$p = p_1 - x(p_1 - p_2)/d \quad (3)$$

where x , the coordinate in the direction of d , is taken to be zero at the face where $p = p_1$. The flux equation corresponding to (3) and following from

$$\frac{dq}{dt} = -\frac{D}{\beta} A \frac{dp}{dx} \quad (4)$$

frequently referred to as Fick's Law,³ is then

$$\frac{dq}{dt} = \frac{D}{\beta} A \frac{p_1 - p_2}{d} \quad (5)$$

Equations (3) and (5) are the ones employed by all investigators previously quoted. Before the applicability of (5) is discussed, it will be shown how this equation is modified to apply to a semicircular rather than a straight tube.

This may be done in several ways, the following one being taken for its combined brevity and rigor. The problem is illustrated in figure 3. At the left side the semicircular tube of rectangular crosssection is pictured, its width (in the direction of the projection) from here on taken to be 1. The inner radius is a and the outer radius b . At one end the partial pressure is p_1 and at the other p_2 . From the picture it appears that, using polar coordinates,

$$\left. \begin{aligned} a &\leq r \leq b \\ -\pi &\leq \theta \leq 0 \end{aligned} \right\} \quad (6)$$

If we use now the complex mapping defined by

$$z = x + iy = re^{i\theta} \quad (7)$$

we may use the transformation

$$\log z = w \quad (8)$$

in which

$$w = u + iv \quad (9)$$

Combination of (7), (8), and (9) gives

$$\left. \begin{aligned} u &= \log r \\ v &= \theta \end{aligned} \right\} \quad (10)$$

from which it follows that

$$\left. \begin{aligned} \log a &\leq u \leq \log b \\ -\pi &\leq v \leq 0 \end{aligned} \right\} \quad (11)$$

³ This is the fundamental expression and is founded on experimental evidence, like Darcy's or Ohm's Law. Expression (1) may be derived in the usual manner from (4).

and that the picture at the right is the conformal mapping to the picture on the left. From (3) it is easily seen that for the righthand map the solution is

$$p = p_1 - v(p_1 - p_2)/\pi \quad (12)$$

and the flux becomes

$$\frac{dq}{dt} = \frac{D}{\beta} \log(b/a) \frac{p_1 - p_2}{\pi} \quad (13)$$

But this expression is then also the solution for the left part of figure 3, since it contains only constants. It should be noted that the formula is for a unit width of tube.

In the following, the discussion is developed for a straight tube again, for the sake of simplicity.

In the experimental setup used by Penman (9) and ourselves, we have a tube with constant partial pressures of vapor on each side and closed at one end. If the partial pressure of the vapor at the open end is made zero by ex-

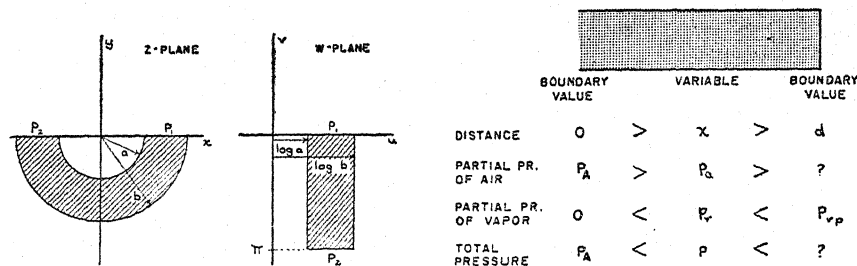


FIG. 3 (left). THE CONFORMAL TRANSFORMATION

FIG. 4 (right). SCHEMATIC REPRESENTATION OF THE STRAIGHT-TUBE PROBLEM

perimental conditions, the situation is illustrated in figure 4. The tube is taken to have a unit cross-sectional area, and its length is d .

As has been indicated, the derivation must take into account the fact that the diffusion of air from the open to the closed end is offset by a sensible flow in the opposite direction, carrying vapor with it. Here, the pattern and notation of the derivation by Nusselt (8) and Jakob (5), are utilized, but we wish to introduce the complication that, as the air-vapor mixture flows toward the open end through the porous medium, it will undergo friction. This, in turn causes the total pressure P to be not constant, as Nusselt and Jakob took it to be, but variable and increasing with the distance from the open end.

Referring to the list of symbols for their meaning, we proceed as follows. The total transport of air has to be zero, and therefore

$$0 = uc_a + D \frac{dc_a}{dx} \quad (14)$$

The measured transport of vapor is due to diffusion and the flow of the mixture and is

$$Q_v = uc_v + D \frac{dc_v}{dx} \quad (15)$$

Going from concentrations to partial pressures with aid of

$$c = \frac{p}{RT} \quad (16)$$

equations (14) and (15) become

$$0 = up_a + D \frac{dp_a}{dx} \quad (17)$$

$$Q_v R_v T = up_v + D \frac{dp_v}{dx} \quad (18)$$

Utilizing $p_a + p_v = P$, (17) and (18) add up to

$$Q_v R_v T = uP + D \frac{dP}{dx} \quad (19)$$

Now we make use of Darcy's Law for flow of gases at small pressure gradients and laminar flow [compare Kirkham (6)],

$$u = \frac{k}{\mu} \frac{dP}{dx} \quad (20)$$

It follows that u may be eliminated, with the result that

$$Q_v R_v T = \frac{k}{\mu} \frac{PdP}{dx} + D \frac{dP}{dx} \quad (21)$$

Integrating and using the boundary condition (fig. 4) that at $x = 0$, $P = P_A$, yield

$$Q_v R_v T x = \frac{k}{\mu} \frac{(P^2 - P_A^2)}{2} + D(P - P_A) \quad (22)$$

Two more boundary conditions remain, namely, at $x = d$, $p_v = p_{vp}$, and at $x = 0$, $P = P_A$, and $p_a = P_A$. These can be utilized by again considering equation (17). Combination with (20) gives

$$0 = \frac{k}{\mu} \frac{dP}{dx} + D \frac{1}{p_a} \frac{dp_a}{dx} \quad (23)$$

Integration, if $P = P_A$, $p_a = P_A$, results in

$$0 = \frac{k}{\mu} (P - P_A) + D \log \frac{p_a}{P_A} \quad (24)$$

and this is identical with:

$$0 = \frac{k}{\mu} (P - P_A) + D \log \frac{P - p_v}{P_A} \quad (25)$$

Consider equation (22) again. The system (25) - (22) becomes, if the condition at $x = d$, $p_v = p_{vp}$ is used:

$$0 = \frac{k}{\mu} (P_d - P_A) + D \log \frac{P_d - p_{vp}}{P_A} \quad (26)$$

$$Q_v R_v T d = \frac{k}{\mu} \frac{(P_d^2 - P_A^2)}{2} + D(P_d - P_A) \quad (27)$$

Note that the boundary condition is applied before the system is resolved into one equation. The remaining unknown, P_d , may now be eliminated with the aid of the two approximations

$$P_d + P_A \approx 2P_A$$

$$\log \frac{P_d - p_{vp}}{P_A} \approx \log \frac{P_A - p_{vp}}{P_A}$$

These approximations will be valid only if p_{vp} is small compared with P_A . Equations (26) and (27) then become

$$(P_d - P_A) = -D \frac{\mu}{k} \log \frac{P_A - p_{vp}}{P_A} \quad (28)$$

and

$$Q_v R_v T d = \frac{k}{\mu} (P_d - P_A) P_A + D (P_d - P_A) \quad (29)$$

Elimination of ($P_d > P_A$) yields, for our result,

$$Q_v R_v T d = \log \frac{P_A - p_{vp}}{P_A} \left(-P_A D - \frac{D^2 \mu}{k} \right) \quad (30)$$

It is seen immediately that (30) reduces to Jakob's formula (5, p. 601, eq. 28-56) if $k = \infty$, D and μ being kept the same.

The next step is to evaluate, for practical purposes, the significance of the difference between formula (30) and Jakob's formula. This may be done readily by comparing the magnitudes of $P_A D$ and $D^2 \mu / k$. In our experiments ethyl alcohol was used, for which at 20°C., $D_0 = 0.120$ cm.²/second (I.C.T.). From Penman's results we may then say that $D = 0.66 D_0 = 0.0792$ cm.²/second. Taking P_A as 760 mm., $P_A D$ is equal to 60.2 mm. cm.²/second. By using the same values for k and μ as were used previously, namely 10 darcys and 1.8×10^{-2} centipoise, $D^2 \mu / k$ is found to be 1.13×10^{-5} atm. cm.²/second, or 8.59×10^{-4} mm. cm.²/second. This constitutes an error of 0.0014 per cent and may be neglected, which is fortunate, since (30) is very unwieldy for the calculation of D , the final objective. Actually, the mixture with the lowest permeability used in our experiments had a permeability of 3.0 darcys, well above the tolerable limit.

In view of the foregoing, it appears that the simpler form of (30) may be used for calculation of experimental data:

$$Q_v R_v T d = -P_A D \log \frac{P_A - p_{vp}}{P_A} \quad (31)$$

It is seen by inspection that equation (5), which is the one commonly used by investigators so far, may be written in the notation of (31) as

$$Q_v R_v T d = D p_{vp} \quad (32)$$

and the necessity of using (31) instead of (32) can be evaluated by comparing the magnitudes of $-P_A \log (P_A - p_{vp}) / P_A$ and p_{vp} . Taking for ethyl alcohol and 20°C. the value $p_{vp} = 44.0$ mm. (I.C.T.), and for P_A 760 mm., the value of

$-P_A \log (P_A - p_{vp})/P_A$ is 44.6 mm. This constitutes an error of about 2 per cent. At higher temperatures, however, because of the rapidly increasing values of the vapor pressure, the error increases: for instance, at 25°C., it is 4 per cent, and at 30°C. it is 7 per cent.

The conclusion is drawn, therefore, that it is preferable to use formula (31) over (32), even when working with a material with a relatively low vapor pressure like ethyl alcohol. It is apparent without further calculations that employment of (32) for experiments with CS_2 would lead to even larger errors than those computed here for ethyl alcohol.

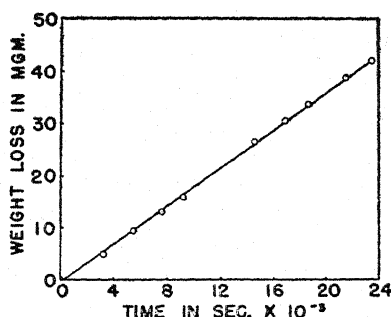


FIG. 5. DECREASE IN WEIGHT OF THE EVAPORATING TUBE WITH TIME IN A TYPICAL EXPERIMENT

It remains now only to write (31) in usable form for the experiments described in the section on procedure. First, equation (31) is rearranged to

$$\frac{dq}{dt} = -\frac{D}{\beta} \cdot \frac{P_A \log [(P_A - p_{vp})/P_A]}{d} \quad (33)$$

From comparison with equation (13) and inspection, it follows that for a semi-circular tube with rectangular cross-section $w(b - a)$, the proper expression is

$$\frac{dq}{dt} = -\frac{D}{\beta} \frac{w \log (b/a) \cdot P_A \log [(P_A - p_{vp})/P_A]}{\pi} \quad (34)$$

In our case $w = 2.54$ cm., $b = 5.08$ cm., and $a = 2.54$ cm., which result in the final expression for D :

$$D = -\frac{dq/dt \cdot 3.141 \cdot \beta}{0.693 \cdot 2.54 \cdot P_A \log [(P_A - p_{vp})/P_A]}$$

This is the equation already given.

Use of the formula can be illustrated by specific data on one of the experiments. To facilitate the calculations, a chart was prepared giving the three quantities p_{vp} , D_0 , and β at 100 per cent porosity, for ethyl alcohol as a function of the temperature. By weighing the container before and after it was filled, the porosity of the material was found to be 35.5 per cent. The experiment extended from 9:30 a.m. until 4:30 p.m., observations being made every half hour. The vapor transfer versus time is plotted in figure 5, which shows that

the process is strictly linear with time. From the slope of the line, dq/dt is found⁴ as 1.785×10^{-3} mgm./second. The average temperature in the liquid during the experiment was 21.8°C., varying between a maximum of 22.2° and a minimum of 21.4°. The corresponding value of p_{vp} is 49.0 mm., of β is 398/0.355 mm. cc./mgm. and of D_0 is 0.1216 cm.²/second. The average atmospheric pressure was 754 mm., with a maximum of 756 and a minimum of 753. Therefore, the value of $\log[(P_A - p_{vp})/P_A]$ is 0.0672 and the calculation becomes:

$$D_{21.8^\circ} = \frac{1.785 \times 10^{-3} \times 3.1416 \times 398}{2.54 \times 0.693 \times 0.355 \times 754 \times 0.0672} = 0.0706 \text{ cm.}^2/\text{second}$$

It follows then that: $D/D_0 = 0.581$.

D needs no correction for pressure, although, paradoxically, it varies linearly with pressure. The reason is that β is taken for normal pressure and not for actual pressure. Since β varies also linearly with pressure (see list of symbols) the correction is made automatically. This has been overlooked sometimes in earlier work.

TABLE 1
Ratio D/D_0 for diffusion of alcohol through air in three different porous media

COMPOSITION OF MEDIUM	POROSITY	D/D_0	STANDARD ERROR OF MEAN
Ungraded quartz sand.....	.415	.589	.003
50% soil < 0.10 mm.355	.577	.003
50% quartz 0.25-0.50 mm.			
3 mm. glass spheres250	.499	.005
quartz sand 0.25-0.50 mm.			

EXPERIMENTAL RESULTS AND DISCUSSION

The composition of the porous media and the values obtained for the ratio D/D_0 are listed in table 1. The quartz sand consisted approximately of 4 per cent grains larger than 1.00 mm., 70 per cent between 0.50 and 1.00 mm., 15 per cent between 0.25 and 0.50 mm., 10 per cent between 0.10 and 0.25 mm., and 1 per cent smaller than 0.10 mm. The soil separate was screened from Ruston coarse sandy loam and consisted mainly of the silt and clay content. The glass spheres were packed as close as possible and then the fine sand was made to fill the interstitial voids by tapping the container.

The difference between the first two figures for D/D_0 in table 1 is statistically not significant. The conclusion is drawn, therefore, that for soil or sand mixtures there exists a constant ratio of the diffusivity of gases and vapors to the diffusivity in a gaseous phase in the range of porosity between 0.10 and 0.60 [concluded from Penman's data (9)] and that the numerical value of this ratio is 0.58 (based on our observations). In spite of all precautions, the experiment

⁴ In the list of symbols q and β are defined in units of grams, rather than milligrams, but the usage here is better adapted to the nature of the experiment. The substitution has no effect on the final result.

has elements of uncertainty especially in regard to the method of packing the material in the container. The fact that agreement was good in the experiment described does not mean that with different kinds of porous materials exactly the same result would be found. For practical purposes it seems more satisfactory to set the value of D/D_0 at 0.6.

If the value for D/D_0 of 0.66 as found by Penman is recalculated by means of the formula given here (which in absence of exact temperature data is only approximately possible), the recalculated value agrees much better with the values obtained here. This would also indicate that the correction for grid impedance in this earlier work was well taken.

The experimental results of Penman and ourselves have recently been confirmed by a theoretical treatment given by De Vries (3). In the porosity range from 10 to 40 per cent his curve for cylindrical particles with blocked pores gives $D = 0.62 D_0$, which is reasonably close to the experimental values.

The values obtained for the glass-sphere-sand system (0.499) deviates considerably from the others. Although it is apparent that this system is quite different in internal geometry, a good reason for its deviating behavior is not obvious.

The theoretical treatment of gaseous diffusion, as presented, is correct only for ideal gases. A rigorous treatment would require use of a modified gas law instead of (16) and use of fugacity instead of partial pressure. Under the prevailing conditions, however, the errors incurred by using the present procedure are insignificant.

SUMMARY

A method is proposed to measure the diffusivity of vapors through porous media, in which the necessity for corrections of estimated value has been eliminated. A formula for calculating the diffusivity is given, based on a theoretical treatment of the experiment and including features which so far have been neglected. The latter are the existence of a gas current to the open end of a tube out of which vapor diffuses and the friction incurred by such a current as it flows through a porous medium. The influence of the latter phenomenon is found to be negligible.

Experimental results have mostly corroborated earlier work but show that the ratio between diffusivity in a porous medium and in gaseous phase is somewhat lower than it was heretofore thought to be, namely, of the order 0.6.

REFERENCES

- (1) BUCKINGHAM, E. 1904 Contributions to our knowledge of the aeration of soils. U. S. Dept. Agr. Bur. Soils Bul. 25.
- (2) CHILDS, E. C., AND GEORGE, N. C. 1950 The control of soil water. *Advances in Agron.* 2: 233-272.
- (3) DE VRIES, D. A. 1950 Some remarks on gaseous diffusion in soils. *Trans. 4th Internatl. Cong. Soil Sci.* 2: 41-43.
- (4) HAGAN, R. M. 1941 Movement of carbon disulfide vapor in soils. *Hilgardia*. 14: 83-118.
- (5) JAKOB, M. 1949 Heat Transfer, vol. 1. J. Wiley and Sons, New York.

- (6) KIRKHAM, D. 1947 Field method for determination of air permeability of soil in its undisturbed state. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 93-99.
- (7) MUSKAT, M. 1937 *The Flow of Homogeneous Fluids Through Porous Media.* McGraw-Hill, New York.
- (8) NUSSELT, W. 1930 Wärmeübertragung, Diffusion und Verdunstung. *Ztschr. Angew. Math. u. Mech.* 10: 105-121.
- (9) PENMAN, H. L. 1940 Gas and vapour movements in the soil: I. *Jour. Agr. Sci.* 30: 437-462.
- (10) PENMAN, H. L. 1940 Gas and vapour movements in the soil: II. *Jour. Agr. Sci.* 30: 570-581.
- (11) POCHETTINO, A. 1914 Su gli elementi cinetici molecolari dei vapori dei composti isomeri. *Nuevo Cimento* 8: 5-36.
- (12) RANEY, W. A. 1950 Field measurements of oxygen diffusion through soils. *Soil Sci. Soc. Amer. Proc.* (1949) 14: 61-65.
- (13) RUSSELL, M. B. 1950 A simplified air-pycnometer for field use. *Soil Sci. Soc. Amer. Proc.* (1949) 14: 73-76.
- (14) SMITH, F. B., AND BROWN, P. E. 1933 Diffusion of carbon dioxide through soils. *Soil Sci.* 35: 413-423.
- (15) TAYLOR, S. A. 1950 Oxygen diffusion in porous media as a measure of soil aeration. *Soil Sci. Soc. Amer. Proc.* (1949) 14: 55-61.
- (16) VAN BAVEL, C. H. M. 1951 A soil aeration theory based on diffusion. *Soil Sci.* 72: 33-46.

A NUMERICAL METHOD FOR SOLVING THE FLOW EQUATION FOR WATER IN UNSATURATED MATERIALS

ARNOLD KLUTE

Cornell University¹

Received for publication July 27, 1951

DEVELOPMENT OF THE FLOW EQUATION

From the equation of continuity and Darcy's law it is possible to derive an equation for the flow of water in an unsaturated porous medium. The equation of continuity is a statement of the principle of conservation of matter and may be written, for an unsaturated porous medium, as:

$$\frac{\partial}{\partial t} (\rho_s \theta) = -\nabla \cdot V \quad (1)$$

where ρ_s is the bulk density of the medium, θ is its moisture content on a dry weight basis, and V is the mass flux of moisture, that is, the mass of fluid flowing through unit cross-section normal to the line of flow in unit time. Darcy's law for the motion of water in a porous system may be expressed as:

$$v = -K \nabla \Phi \quad (2)$$

where $-\nabla \Phi$ is the negative gradient of the total moisture potential, v is the volume flux of moisture, and K is the coefficient of aqueous conductivity. The mass flux, V is simply the product of the fluid density and the volume flux, v . With this in mind, equations (1) and (2) may be combined to yield the following equation of flow for water in an unsaturated system:

$$\frac{\partial}{\partial t} (\rho_s \theta) = \nabla \cdot (\rho K \nabla \Phi) \quad (3)$$

where ρ is the fluid density. If the total moisture potential is considered as the sum of the pressure and gravitational potentials, then for a system in which flow is occurring in the vertical direction only, we have:

$$\rho_s \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(\rho K \frac{\partial \psi}{\partial z} \right) + \frac{\partial}{\partial z} (\rho K g) \quad (4)$$

where ψ is the pressure potential, or "capillary potential" as it is usually called, and g is the gravitational constant. If θ and ψ may be considered to be related by a single-valued function, then equation (4) may be put in the form:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial \theta}{\partial z} \right) + \frac{\rho}{\rho_s} g \frac{\partial K}{\partial z} \quad (5)$$

¹ Part of a thesis submitted to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of doctor of philosophy. The author acknowledges with appreciation the assistance of M. B. Russell, who supervised his studies.

In this equation the diffusivity, D , is given by $\frac{\rho}{\rho_s} K \frac{\partial \psi}{\partial \theta}$, where both K and $\frac{\partial \psi}{\partial \theta}$ are considered functions of the moisture content of the medium. The reciprocal of the term $\frac{\partial \psi}{\partial \theta}$ is analogous to the specific heat in the theory of heat flow. It is proposed to call this term the "specific moisture capacity."

It would be desirable to obtain a general analytical solution of equation (5), but the complication introduced by the dependence of the conductivity and specific moisture capacity on the moisture content of the medium seems to prevent this. Accordingly, numerical or graphical methods must be used. To solve the flow equation, the functional dependence of the conductivity and specific moisture capacity on the moisture content of the medium must be known. The former may be obtained by the methods used by Moore (5), or Richards (6) and Christiansen.² The specific moisture capacity, $\frac{\partial \theta}{\partial \psi}$, is the first derivative of a desorption curve for the material, that is, a plot of θ vs. ψ .

ITERATIVE METHOD FOR SOLVING FLOW EQUATION

The following development is based upon a method used in diffusion of organic solvents into polymer films and fibers (4). The general equation of flow may be put into the form of the nonlinear diffusion equation if we restrict ourselves to a consideration of horizontal flow. In this case, equation (5) becomes:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \theta}{\partial x} \right) \quad (6)$$

First let us consider a semi-infinite system with the following boundary and initial conditions:

$$\begin{aligned} \theta &= \theta_0 & @ \ x &= x_0 & t > 0 \\ \theta &= \theta_1 & @ \ t &= 0 & x > 0 \end{aligned} \quad (7)$$

It will be convenient to introduce nondimensional variables as follows:

$$c = \frac{\theta}{\theta_0} \quad \zeta = \frac{x}{x_0} \quad \tau = \frac{D_0 t}{x_0^2} \quad D = \frac{D(\theta)}{D_0} \quad (8)$$

The subscript 0 indicates a reference value of the quantity to which it is attached. Substitution of these variables into equations (6) and (7) gives:

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial \zeta} \left(D \frac{\partial c}{\partial \zeta} \right) \quad (9)$$

$$\begin{aligned} c &= 1 & @ \ \zeta &= 0 & \tau > 0 \\ c &= c_1 & @ \ \tau &= 0 & \zeta > 0 \end{aligned} \quad (10)$$

² CHRISTIANSEN, H. R. Flow of fluids in porous media. 1940. [Unpublished doctor's thesis. Copy on file Iowa State College Library, Ames.]

Following a method which was apparently first used by Boltzman (1), we introduce a variable defined as follows:

$$\eta = \frac{\xi}{2\tau^{1/2}} \quad (11)$$

Substitution of this variable into equations (9) and (10) leads to the following differential equation:

$$-2\eta \frac{\partial c}{\partial \eta} = \frac{\partial}{\partial \eta} \left(D \frac{\partial c}{\partial \eta} \right) \quad (12)$$

In terms of the new variable the boundary conditions are:

$$\begin{aligned} c &= 1 & \eta &= 0 \\ c &= c_1 & \eta &\rightarrow \infty \end{aligned} \quad (13)$$

Equation (12) may be integrated to yield the following result:

$$c = 1 - A \int_D^1 e^{-\int (2\eta/D) d\eta} d\eta \quad (14)$$

where A is a constant determined by the boundary and initial conditions.

A method of iteration may be used to evaluate c as a function of x and t . As a first approximation to c we use the solution of equation (9) in which D is regarded constant. This solution is:

$$c = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\eta/D^{1/2}} e^{-\beta^2} d\beta \quad (15)$$

This equation and an expression for D as a function of c may be used in an iterative process to obtain numerical solutions of equation (12). We may write:

$$D = \frac{D(\theta)}{D_0} = 1 - f(c) \quad (16)$$

The function denoted in equation (16) may be given analytically or numerically. The iteration process proceeds as follows:

1. From a given $D(\theta)$ calculate D by means of equation (16). Plot D against c where $c = \theta/\theta_0$.
2. Tabulate values of η which are conveniently spaced, perhaps every 0.1 in η , over a range such that c as given by equation (15) becomes essentially zero at the upper limit of η .
3. Calculate c by equation (15) for each value of η .
4. From the graph of D vs. c read off the values of D corresponding to the values of c as calculated in step 3. This does not have to be done graphically; it may be done by interpolation from a table of D vs. c .
5. Using the values of D so obtained, calculate c by means of equation (14). The constant A is to be taken such that c will equal zero when $\eta = \eta_{\text{lim}}$ where η_{lim} is the largest value of η .
6. Interpolate, either graphically or numerically, values of D corresponding to each c as calculated in step 5. Using these new values of D , repeat step 5 until successive values of c at a given η agree within the limits of the allowable error.

If $c = 0$ at the upper limit of η used, but $dc/d\eta$ is not zero, then the iteration process must be extended to higher values of η . In place of equation (15), other solutions of equation (12) for appropriate boundary conditions may be used to start the iteration process. The procedure is the same, except that at the upper value of η the value of c may not necessarily be zero. If, for example, c equals c_1 initially in the system, then at η_{lim} we should have c equal to c_1 and $dc/d\eta$ equal to zero.

A few remarks should be made about the determination of A , the constant in equation (14). If the boundary conditions are:

$$c = 1 \quad \eta = 0$$

$$c = c_1 \quad \eta \rightarrow \infty$$

then in practice the limit $\eta \rightarrow \infty$ can be replaced by $\eta \rightarrow \eta_{\text{lim}}$ where η_{lim} is a finite value of η sufficiently large so that at η_{lim} we have:

$$c = c_1 \quad \frac{\partial c}{\partial \eta} \cong 0.$$

The constant, A , is given by:

$$A = \frac{1 - c_1}{\int_0^{\eta_{\text{lim}}} \frac{1}{D} e^{-2 \int (\eta/D) d\eta} d\eta} \quad (17)$$

For $D(\theta)$ functions which vary widely, the convergence of the above iteration process is slow. A better first approximation to the solution is needed. In steady state flow the product $\left[D(\theta) \frac{\partial \theta}{\partial x} \right]$ is constant at all points of the system. In the nonsteady state this product may not be constant, but still it may be sufficiently near to a constant that the solution expressed in terms of a variable which includes this product may be simpler in form. Accordingly define a variable s by the relation:

$$s = \int_0^c D dc / \int_0^1 D dc \quad (18)$$

Let:

$$\int_0^1 D dc = D_1$$

Then:

$$\frac{ds}{d\eta} = \frac{D}{D_1} \frac{dc}{d\eta} \quad (19)$$

Crank and Henry (4) made the following comments on the shape of the $s - \eta$ curves: When the curves were plotted they all had the same general shape. They were straight lines over the range $1 > s > 0.2$ with a gradient of approximately $-\frac{2}{\sqrt{\pi D_1}}$. This is the gradient the curves would have at $\eta = 0$ if $D = D_1$ and were constant.

These remarks suggest that the following first approximation to s will be useful. For $s > 0.2$, assume a linear relation with a gradient of $-\frac{2}{\sqrt{\pi D_1}}$. Below $s = 0.2$, tail s off to approach zero asymptotically at a value of η slightly greater than that at which the straight line intersects the η axis.

In terms of the variable s , equation (14) becomes:

$$s = 1 - A \int_0^\eta e^{-\int^{(2\eta/D)} d\eta} d\eta \quad (20)$$

The iterative treatment of this equation to obtain s as a function of η when D is known as a function of c is similar to that for equation (14). The first approximation to s as a function of η is obtained as already outlined. As before, tabulate values of η ; obtain the corresponding values of s from the first approximation already described; and find the values of D corresponding to each s . Using these values of D , calculate s by means of equation (20). Then obtain a new set of values of D for each s and repeat the use of equation (20). This cycle is repeated until successive values of s agree within the limits of allowable error. When the values of s agree reasonably well it is best to convert them to c values and finish the iteration in terms of c .

APPLICATION AND DISCUSSION

This method was applied to the following problem. A horizontal semi-infinite column of $\frac{1}{2}$ - $\frac{1}{4}$ mm. sand was assumed to have an initially constant moisture content of 0.01 gm./gm. The end at $x = 0$ was considered to be maintained at saturation, $\theta = 0.357$ gm./gm. The conductivity moisture content function calculated according to Childs' method (2) and the specific moisture capacity moisture content function from a desorption curve were used to calculate $D(\theta)$. These data are given in table 1. The initial distribution of the function s as defined by equation (18) is shown in figure 1. The iterative procedure was carried on in terms of the variable s for two cycles. Then the values of s were converted to values of c by means of the data in table 2 and the iterative process continued until successive values of c were in approximate agreement. The final distribution of c with η is shown in figure 2. The calculations are abstracted in tables 3 and 4. After the fifth cycle of the calculations the successive values of c were in sufficiently close agreement. A plot of moisture content against distance along the column is shown in figure 3.

The interesting result of these calculations is the locally steep gradient of moisture content, that is, a wetting front. Thus, it would seem that, if one considers the variation of conductivity and the specific moisture capacity with moisture content, the phenomenon of a wetting front is predicted by the theory. It also appears from past experience with this material, however, that the wetting front advances too rapidly. Another apparent difficulty is that the gradient of moisture content in the zone of the wetting front, as calculated by the numerical procedure, decreases too rapidly as the wetting front advances along the column. These difficulties probably have their origin in the complica-

TABLE 1

Aqueous conductivity, specific moisture capacity, and diffusivity as functions of the moisture content

MOISTURE CONTENT	CONDUCTIVITY	SPECIFIC MOISTURE CAPACITY	DIFFUSIVITY
<i>gm./gm.</i>	<i>sec.</i>	<i>cm.²/sec.²</i>	
0.357	1.00×10^{-4}	0.45×10^{-6}	2.22×10^2
0.354	0.985×10^{-4}	1.11×10^{-6}	8.87×10^1
0.352	0.955×10^{-4}	1.52×10^{-6}	6.29×10^1
0.348	0.941×10^{-4}	2.10×10^{-6}	4.48×10^1
0.343	0.911×10^{-4}	3.20×10^{-6}	2.76×10^1
0.337	0.876×10^{-4}	4.00×10^{-6}	2.19×10^1
0.330	0.834×10^{-4}	5.00×10^{-6}	1.67×10^1
0.320	0.790×10^{-4}	6.80×10^{-6}	1.16×10^1
0.300	0.730×10^{-4}	28.0×10^{-6}	2.61
0.235	0.470×10^{-4}	34.3×10^{-6}	1.37
0.165	0.230×10^{-4}	28.7×10^{-6}	8.02×10^{-1}
0.125	0.139×10^{-4}	19.3×10^{-6}	7.20×10^{-1}
0.095	0.713×10^{-5}	13.3×10^{-6}	5.36×10^{-1}
0.070	0.307×10^{-5}	9.4×10^{-6}	3.23×10^{-1}
0.055	0.132×10^{-5}	7.0×10^{-6}	1.88×10^{-1}
0.043	0.667×10^{-6}	5.1×10^{-6}	1.33×10^{-1}
0.036	0.323×10^{-6}	3.5×10^{-6}	9.22×10^{-2}
0.031	0.187×10^{-6}	2.4×10^{-6}	7.80×10^{-2}
0.028	0.114×10^{-6}	2.2×10^{-6}	5.18×10^{-2}
0.024	0.785×10^{-7}	1.4×10^{-6}	5.60×10^{-2}
0.021	0.404×10^{-7}	1.1×10^{-6}	3.68×10^{-2}
0.019	0.258×10^{-7}	1.0×10^{-6}	2.58×10^{-2}
0.017	0.126×10^{-7}	0.9×10^{-6}	1.40×10^{-2}
0.015	0.877×10^{-8}	0.8×10^{-6}	1.10×10^{-2}
0.014	0.444×10^{-8}	0.74×10^{-6}	6.0×10^{-3}
0.013	0.241×10^{-8}	0.68×10^{-6}	3.54×10^{-3}
0.012	0.166×10^{-8}	0.62×10^{-6}	2.68×10^{-3}
0.011	0.589×10^{-9}	0.56×10^{-6}	1.05×10^{-3}
0.010	0.263×10^{-9}	0.50×10^{-6}	5.26×10^{-4}

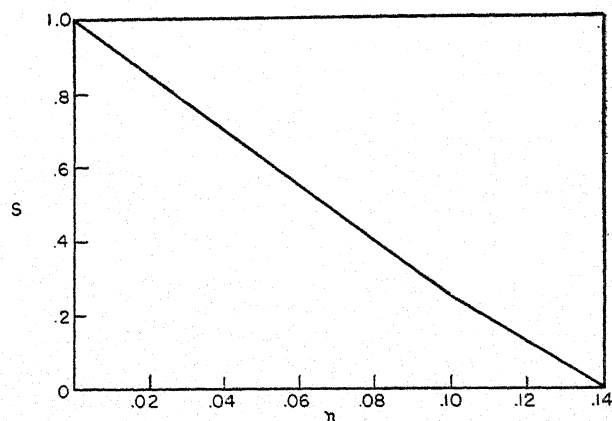


FIG. 1. ASSUMED INITIAL DISTRIBUTION OF s WITH η FOR A SEMI-INFINITE COLUMN OF $\frac{1}{2}$ - $\frac{1}{4}$ MM. SAND

TABLE 2
Calculated dimensionless variables for $\frac{1}{2}$ - $\frac{1}{4}$ mm. sand*

DIFFUSIVITY $D = \frac{D(\theta)}{D_0}$	CONCENTRATION VARIABLES	
	$c = \frac{\theta}{\theta_0}$	$s = \frac{\int_0^c Ddc}{\int_0^1 Ddc}$
1.00	1.00	1.00
3.99×10^{-1}	9.91×10^{-1}	7.40×10^{-1}
2.83×10^{-1}	9.85×10^{-1}	6.35×10^{-1}
2.02×10^{-1}	9.75×10^{-1}	5.44×10^{-1}
1.24×10^{-1}	9.60×10^{-1}	4.48×10^{-1}
9.87×10^{-2}	9.44×10^{-1}	3.72×10^{-1}
7.53×10^{-2}	9.24×10^{-1}	2.98×10^{-1}
5.22×10^{-2}	8.96×10^{-1}	2.22×10^{-1}
1.17×10^{-2}	8.40×10^{-1}	1.46×10^{-1}
6.17×10^{-3}	6.58×10^{-1}	7.72×10^{-2}
3.62×10^{-3}	4.62×10^{-1}	3.63×10^{-2}
3.24×10^{-3}	3.50×10^{-1}	2.00×10^{-2}
2.42×10^{-3}	2.66×10^{-1}	9.88×10^{-3}
1.45×10^{-3}	1.96×10^{-1}	4.10×10^{-3}
8.47×10^{-4}	1.54×10^{-1}	2.05×10^{-3}
5.99×10^{-4}	1.20×10^{-1}	1.00×10^{-3}
4.15×10^{-4}	1.01×10^{-1}	5.90×10^{-4}
3.52×10^{-4}	8.68×10^{-2}	3.58×10^{-4}
2.33×10^{-4}	7.85×10^{-2}	2.72×10^{-4}
2.52×10^{-4}	6.72×10^{-2}	1.55×10^{-4}
1.66×10^{-4}	5.88×10^{-2}	8.03×10^{-5}
1.16×10^{-4}	5.32×10^{-2}	4.67×10^{-5}
6.30×10^{-5}	4.76×10^{-2}	2.52×10^{-5}
4.95×10^{-5}	4.20×10^{-2}	1.19×10^{-5}
2.70×10^{-5}	3.92×10^{-2}	7.30×10^{-6}
1.59×10^{-5}	3.64×10^{-2}	4.74×10^{-6}
1.21×10^{-5}	3.36×10^{-2}	2.83×10^{-6}
4.73×10^{-6}	3.08×10^{-2}	1.83×10^{-6}
2.73×10^{-6}	2.80×10^{-2}	1.41×10^{-6}
0.0	0.00	0.00

* $D_0 = 2.22 \times 10^2$; $\theta_0 = 0.357$.

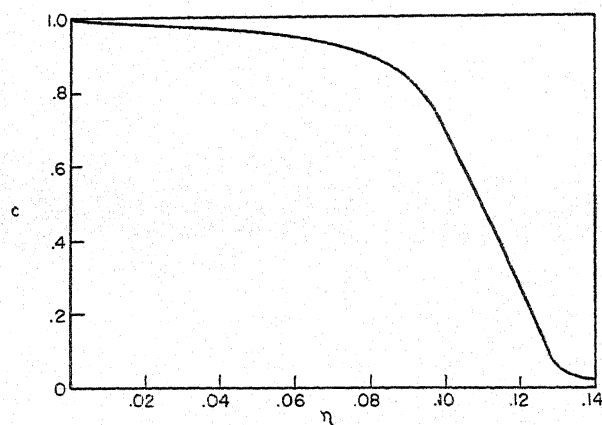


FIG. 2. FINAL CALCULATED DISTRIBUTION OF c WITH η FOR A SEMI-INFINITE COLUMN OF $\frac{1}{2}$ - $\frac{1}{4}$ MM. SAND

TABLE 3

Summary of the first cycle of calculations in the iterative procedure

η	s	D	$-\int_D^{2\eta} d\eta$	$-\int_e^{2\eta} d\eta$	$\int_e^{-\int_D^{2\eta} d\eta} d\eta$	$s = 1 - \frac{A}{\int_e^{-\int_D^{2\eta} d\eta} d\eta}$
0.00	1.00	1.00	0.00	1.00	0.000	1.00
0.01	0.926	0.76	0.000132	1.00	0.010	0.917
0.02	0.852	0.588	0.000604	1.00	0.020	0.833
0.03	0.778	0.457	0.00160	0.9984	0.0299	0.750
0.04	0.704	0.355	0.00338	0.9966	0.0399	0.667
0.05	0.630	0.263	0.00641	0.9936	0.0499	0.585
0.06	0.556	0.209	0.0112	0.989	0.0598	0.501
0.07	0.482	0.145	0.0189	0.981	0.0697	0.421
0.08	0.408	0.107	0.0312	0.969	0.0794	0.339
0.09	0.332	0.085	0.0493	0.952	0.0890	0.257
0.10	0.258	0.537	0.108	0.898	0.0983	0.131
0.11	0.194	0.0269	0.227	0.797	0.1067	0.111
0.12	0.130	0.0105	0.382	0.682	0.1141	0.050
0.13	0.066	0.00536	0.739	0.478	0.1199	0.020
0.14	0.00	0.00				

$$A = \frac{1 - s_{\text{lim}}}{\int_e^{-\int_D^{2\eta} d\eta} d\eta} = \frac{1 - 0}{0.1199} = 8.35$$

TABLE 4

Successive approximations in the iterative calculation of the moisture content distribution in $\frac{1}{2}$ - $\frac{1}{4}$ mm. sand, absorption problem

η	s			c			
	1st*	2nd*	3rd*	3rd*	4th*	5th*	6th*
0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.01	0.926	0.917	0.911	0.995	0.997	0.997	0.997
0.02	0.852	0.833	0.833	0.990	0.991	0.992	0.994
0.03	0.778	0.750	0.735	0.989	0.985	0.986	0.989
0.04	0.704	0.667	0.647	0.093	0.078	0.978	0.981
0.05	0.630	0.585	0.559	0.975	0.968	0.966	0.971
0.06	0.556	0.501	0.470	0.963	0.955	0.955	0.956
0.07	0.482	0.420	0.384	0.946	0.936	0.930	0.936
0.08	0.408	0.339	0.298	0.925	0.912	0.912	0.906
0.09	0.332	0.257	0.215	0.887	0.870	0.849	0.835
0.10	0.258	0.131	0.135	0.820	0.752	0.701	0.676
0.11	0.194	0.111	0.073	0.647	0.554	0.481	0.455
0.12	0.130	0.050	0.030	0.450	0.324	0.250	0.247
0.13	0.066	0.020	0.012	0.270	0.144	0.065	0.070
0.14	0.00	0.000	0.00	0.028	0.028	0.028	0.028

* Approximation.

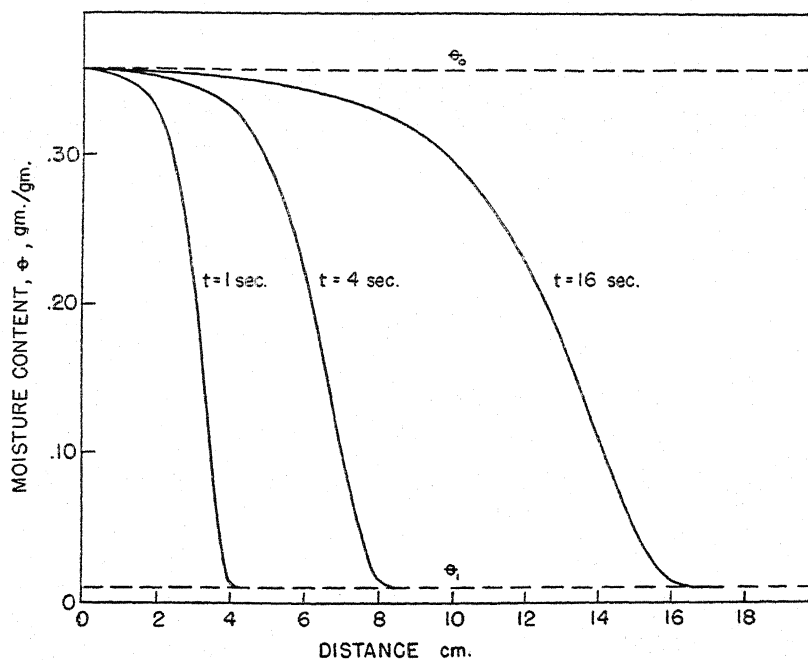


FIG. 3. MOISTURE CONTENT DISTRIBUTION IN A SEMI-INFINITE COLUMN OF $\frac{1}{2}$ - $\frac{1}{4}$ MM. SAND AS CALCULATED BY THE ITERATIVE PROCEDURE—ABSORPTION PROBLEM

TABLE 5

Successive approximations in the iterative calculation of the moisture content distribution in a semi-infinite system, desorption problem

η	s				c	
	1st*	2nd*	3rd*	4th*	4th*	5th*
0.0	0.00	0.00	0.00	0.00	0.550	0.550
0.05	0.068	0.0715	0.0663	0.678	0.602	0.601
0.10	0.136	0.142	0.132	0.134	0.648	0.646
0.20	0.266	0.278	0.257	0.262	0.720	0.722
0.30	0.391	0.401	0.374	0.379	0.792	0.780
0.40	0.511	0.513	0.478	0.485	0.840	0.827
0.50	0.619	0.611	0.570	0.580	0.875	0.866
0.60	0.718	0.698	0.650	0.660	0.903	0.896
0.70	0.796	0.771	0.720	0.728	0.922	0.920
0.80	0.830	0.836	0.777	0.786	0.940	0.937
0.90	0.865	0.889	0.827	0.833	0.955	0.953
1.00	0.895	0.931	0.866	0.872	0.967	0.964
1.20	0.935	0.964	0.926	0.929	0.981	0.981
1.40	0.961	0.981	0.962	0.964	0.992	0.991
1.60	0.980	0.993	0.983	0.982	0.997	0.997
1.80	0.993	0.999	0.995	0.995	0.999	0.999
2.00	1.00	1.00	1.00	1.00	1.000	1.000

* Approximation.

tion of hysteresis, that is, in the fact that a desorption curve was used to calculate D , and in this problem we have an absorption process. It would be more correct to use an absorption curve for the calculation of D to be applied in this case. In spite of these difficulties, the fact that a wetting front is indicated is an improvement over the situation when the diffusivity is considered constant. In the latter case, no wetting front is predicted.

Another problem was set up in which a horizontal semi-infinite column of $\frac{1}{2}$ - $\frac{1}{4}$ mm. sand was assumed to be initially at a constant moisture content, θ_2 , and the end at $x = 0$ was considered to be maintained at θ_1 , where $\theta_1 < \theta_2$.

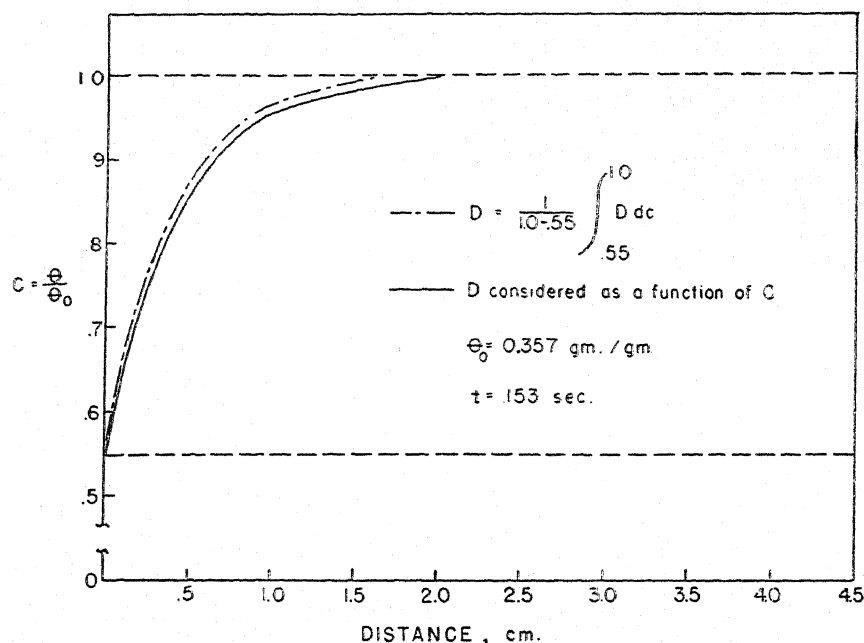


FIG. 4. CALCULATED DISTRIBUTION OF MOISTURE CONTENT IN A SEMI-INFINITE COLUMN OF $\frac{1}{2}$ - $\frac{1}{4}$ MM. SAND—DESORPTION PROBLEM

In terms of the variables c and η , the solution of equation (12) for these conditions is:

$$c = c_1 + A \int \frac{e^{-\int (2\eta/D) d\eta}}{D} d\eta \quad (21)$$

The iterative procedure is very similar to that in the absorption problem. In terms of the variable s , which is here defined as:

$$s = \int_{c_1}^c D dc / \int_{c_1}^1 D dc \quad (22)$$

the solution of equation (12) is:

$$s = k_1 \int_e^{-\int (2\eta/D) d\eta} d\eta \quad (23)$$

for the desorption problem. The initial distribution of s in η and the successive approximations are given in table 5. The distribution of moisture content with distance along the column is shown in figure 4. For comparison, the moisture content distribution as calculated for D constant and equal to the integrated mean over the range of moisture content involved is also shown. There is not much difference in the shape of the curves for constant D and for D as a function of the moisture content. The rate of removal of water in this desorption case seems to be too rapid, but no data are available as to the rate of removal of water from such a system.

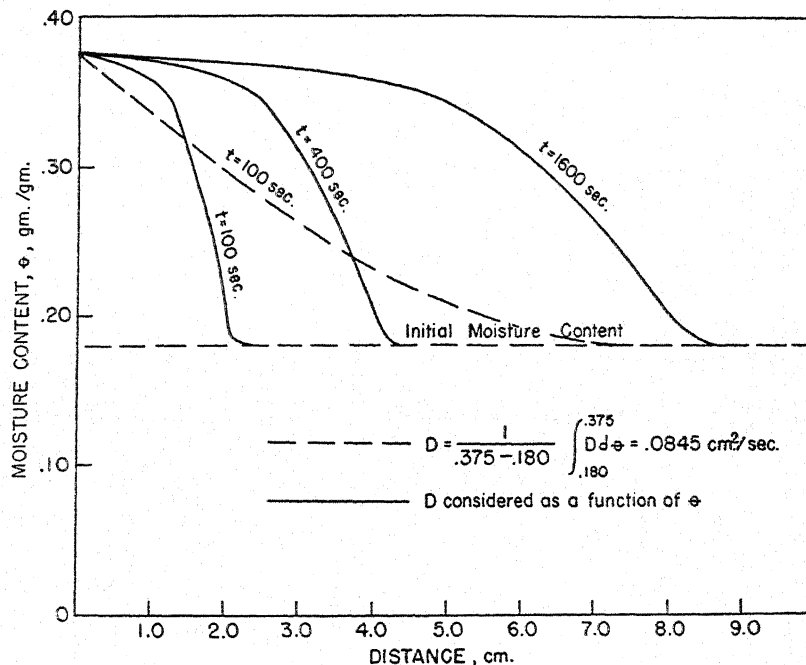


FIG. 5. CALCULATED MOISTURE CONTENT DISTRIBUTION IN A SEMI-INFINITE COLUMN OF YOLO LIGHT CLAY—ABSORPTION CASE

A diffusivity moisture content function was calculated for Yolo light clay from desorption data and conductivity-moisture content data presented by Moore (5). This function was used to calculate the distribution of moisture content in a semi-infinite column of Yolo light clay with an initial moisture content of 18.0 per cent, and the boundary at $x = 0$ maintained at saturation, a moisture content of 37.5 per cent. This distribution is shown in figure 5. For comparison, the distribution for a constant diffusivity equal to the integrated mean diffusivity over the range of moisture content in the sample is also shown.

In general, the iterative procedure seems quite satisfactory. As described, it can only be applied to the nonlinear diffusion equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \theta}{\partial x} \right) \quad (24)$$

which restricts its use to horizontal systems of flow. An iterative process of somewhat different nature may be applied to the flow equation for vertical systems as well as for finite systems. This procedure has been described by Crank and Nicolson (3). Seemingly, it should be possible to adapt this method to the equations involved in moisture flow. Data on the dependence of the diffusivity on the moisture content is lacking, and further work should be done to obtain them. When these data are available, the calculated distributions should be checked against experimentally determined distributions.

SUMMARY

An equation describing the flow of water in unsaturated porous materials was derived from Darcy's law and the equation of continuity. A numerical method of solution of this equation for semi-infinite horizontal systems of flow was described and applied to several examples. The phenomenon of a wetting front was shown to be indicated when the variation of the diffusivity with moisture content was considered.

REFERENCES

- (1) BOLTZMAN, L. 1894 Zur Integration der diffusions Gleichung bei variablen diffusions Coefficienten. *Ann. Phys. [Leipzig]* 53: 959-964.
- (2) CHILDS, E. C., AND GEORGE, N. C. 1950 Permeability of porous materials. *Proc. Roy. Soc. [London]* (A) 201: 392-399.
- (3) CRANK, J., AND NICOLSON, H. 1947 A practical method of numerical evaluation of solutions of partial differential equations of the heat conduction type. *Proc. Cambridge Phil. Soc.* 43: 50-61.
- (4) CRANK, J., AND HENRY, M. E. 1949 Diffusion in media with variable properties: I, II. *Trans. Faraday Soc.* 45: 636-642; 1119-1128.
- (5) MOORE, R. E. 1939 Water conduction from shallow water tables. *Hilgardia* 12: 383-401.
- (6) RICHARDS, L. A. 1930 Capillary conduction of liquids through porous materials. *Physics* 1: 318-333.

PHYTASE ACTIVITY IN SOILS

R. H. JACKMAN AND C. A. BLACK

Iowa Agricultural Experiment Station¹

Received for publication July 10, 1951

Rogers, Pearson, and Pierre (9) found that the concentration of phytate phosphorus in culture solution was reduced by corn and tomato plants without appearance of inorganic phosphorus in the solution. Evidently, hydrolysis of the phytin was not prerequisite to absorption of the phosphorus. If plants possess the ability to absorb phytin without hydrolysis, the presence of phytase in soils is not essential for the utilization of soil phytate phosphorus by plants. It has become evident from recent work of the authors (5), however, that the equilibrium concentration of phytate phosphorus in the soil solution must be considerably lower than is that of inorganic phosphorus. If phytase is present in the soil, therefore, the organic phosphorus of the phytin molecule can be hydrolyzed to the inorganic form, in which condition it can exist at a higher solubility level than is possible before hydrolysis. Such a process should enhance the availability of the phosphorus to plants.

Although it has been observed (8) that with time there is a partial hydrolysis of phytate phosphorus added to soil, there has hitherto been no investigation of phytase activity in soils. The present paper reports a method for measuring phytase activity in soils together with data that show something of the behavior of phytase in soils.

MEASURING PHYTASE ACTIVITY

To 5-gm. samples of soil in each of two 250-ml. Erlenmeyer flasks were added 10 ml. of potassium citrate solution² and 10 drops of toluene. To one of the flasks was added 10 ml. of sodium phytate solution³, and to the other was added 10 ml. of water. The flasks were stoppered, the contents were mixed by swirling gently, and the flasks were incubated at 45° C. for 20 hours. At the end of the incubation, 50 ml. of 4 N HCl was added and the flasks were allowed to stand for 30 minutes. The contents were then filtered on Büchner funnels and washed with five 20-ml. portions of 4 N HCl. If the filtrates were to be analyzed the same day as the filtration, they were diluted to 500 ml. and inorganic phosphorus was determined in an aliquot by the method of Dickman and Bray (2). If the analyses

¹ Contribution from the Iowa Agricultural Experiment Station, the U. S. Department of Agriculture, and the Tennessee Valley Authority. Journal Paper No. J-1968 of the Iowa Agricultural Experiment Station, Ames. The senior author is now at Rukuhia Soil Research Station, Hamilton, New Zealand. The authors are indebted to F. E. Clark for advice and assistance in the investigation and in the preparation of the paper.

² Ten grams of potassium citrate monohydrate dissolved in water, titrated to pH 5 with HCl, and diluted to 100 ml.

³ The original solution of sodium phytate was prepared as described previously (5). For use, it was titrated to pH 5 with HCl, and the concentration of phytate phosphorus was adjusted to 6,000 ppm. It was stored in a refrigerator to inhibit fungal growth.

were to be delayed, the filtrates were neutralized with concentrated NH_4OH and cooled. Before analysis, just enough HCl was added to dissolve the precipitate formed on addition of the NH_4OH . The solutions were then diluted to 500 ml. and analyzed for inorganic phosphorus. In either case, the difference in content of inorganic phosphorus between the filtrate from the soil treated with sodium phytate (after correction for any inorganic phosphorus originally present in the added phytate) and the filtrate from the soil treated with water was taken as a measure of phytase activity in the soil.

Preliminary work showed that no phytase was extracted from soil with water and that phytate added to soil was only slightly hydrolyzed during incubation under conditions favorable for the action of phytase. Since only a small fraction of the added phytate remained in solution in the latter experiments, however, little hydrolysis would be expected even if the soil had considerable phytase activity.

It was possible to retain almost all the phytate in solution at pH 5 in the presence of 61 gm. of potassium citrate monohydrate per 100 ml. of solution, but high citrate concentrations markedly depressed the rate of phytate hydrolysis by phytase. As a compromise, a citrate concentration of 5 gm. per 100 ml. of solution was used. At this concentration, the rate of phytate hydrolysis by phytase in absence of soil was two to three times as great as it was in absence of citrate, in agreement with the observations of Hoff-Jørgensen and Porsdal (4). In presence of soil, however, not all the phytate remained soluble. The proportion of the phytate that remained soluble in different soils was not determined where the solution contained 60 mgm. of phytate phosphorus and 5 per cent potassium citrate, but it was found in an experiment where the solution contained 2 mgm. of phytate phosphorus and 32 per cent potassium citrate that the range of phytate solubility was from 89 to 95 per cent in four acid soils tested. In Clarion silt loam (pH 6.5), about 70 per cent of an added 2 mgm. of phytate phosphorus remained soluble at a citrate concentration of 5 per cent.

There were two reasons for the addition of a large amount of phytate phosphorus (60 mgm. in 20 ml.) in the method for phytase activity. First, the relative amounts of phytate phosphorus in solution were expected to be more nearly constant between soils with a large addition than with the small addition used in the solubility tests. Second, the velocity of an enzyme-catalyzed change is proportional to the enzyme concentration and independent of the substrate concentration if the latter is sufficiently high (7).

Experiments showed that even under the conditions used, the rate of hydrolysis was not entirely independent of the phytate concentration; however, the dependence of hydrolysis on concentration was such that a difference of 10 per cent in the amount of soluble phytate would result in a difference of about 5 per cent in the amount of hydrolysis.

The recovery of added inorganic phosphorus by the procedure used was checked with five soils and was found to be quantitative in four. In a sample of Shelby silt loam C horizon, the recovery was 77 per cent. Since the phosphate-fixing power of the soils used in the following experiments was less than that of some

of the soils giving quantitative recovery of added inorganic phosphorus, the recovery of hydrolyzed phytate phosphorus probably was quantitative.

No investigation of the effect of pH on hydrolysis was conducted, since previous work by the authors (6) and others showed that the maximum rate of phytate hydrolysis by phytase occurs at about pH 5.

The effect of temperature was investigated, and it was found that during an incubation of 20 hours, greater hydrolysis occurred at 45° C. than at either 35° or 55° C. A difference of 2° C. was sufficient to produce a significant difference in the amount of hydrolysis.

The precision of the method was estimated from 19 determinations of phytase activity on subsamples of a single soil sample. Duplicate determinations of inorganic phosphorus were made on each extract. The range in amount of hydrolyzed phytate phosphorus in the extract from the different subsamples was from 0.194 to 0.234 mgm. The mean was 0.208 mgm., and the standard deviation was 0.013 mgm. This precision was considered to be adequate for the purposes at hand.

MICROBIAL AND PHYTASE ACTIVITY

Experimental work on the measurement of phytase activity in soils indicated that such activity could be increased if conditions were made favorable for development of a large population of microorganisms. To determine whether microbial activity is, in fact, related to phytase activity, an investigation was made of the CO₂ production and the phytase activity in soil samples so treated as to produce mixed microbial populations differing in activity. The phytase activity associated with the growth of pure and mixed soil cultures of certain bacteria and fungi was also investigated.

In all series, 100-gm. samples of Clarion silt loam of pH 5.8 were placed in 500-ml. Erlenmeyer flasks with ground plant materials, moistened with water, and steam-sterilized. The samples were then inoculated, and the flasks were incubated at 28° C. During incubation, a stream of sterile, moist, CO₂-free air was passed continually through the flasks and then into NaOH, where the CO₂ was collected and determined by titration in the presence of BaCl₂. Phytase activity in the soil was determined at the end of the incubation period.

In the first series, the inoculant was a water extract of fresh field soil, the moisture content was 25 per cent of the dry weight of the soil, and the plant material was alfalfa meal added in increasing amounts up to 2 per cent of the dry weight of the soil. The phytase activity was determined in the samples as they came from the flasks after 5 days' incubation. The results from this series are shown in figure 1. In the second series, the inoculants were pure or mixed cultures of various fungi, the moisture content was 25 per cent of the dry weight of the soil, and the plant material was alfalfa meal added at a rate of 2 per cent of the dry weight of the soil. The phytase activity was determined in the samples as they came from the flasks after 6 days' incubation. The results from this series are given in table 1. In the third series, the inoculants were pure cultures of various bacteria. Before the determination of phytase activity, the soil samples were

placed under a fan at room temperature and dried until the soil color started to lighten. The soil moisture content during incubation, the organic materials added, and the incubation time are indicated in table 2 together with the results.

Figure 1 shows that phytase activity was essentially directly proportional to the quantity of CO₂ evolved by a mixed population of microorganisms. If CO₂ production is an adequate measure of over-all microbial metabolism, it may be concluded that with increasing microbial metabolism in the soil there was a cor-

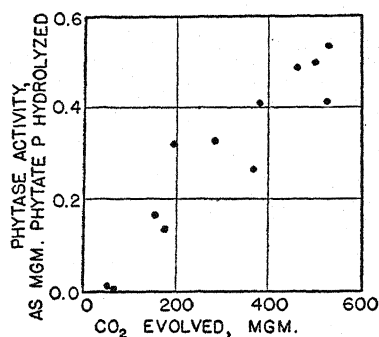


FIG. 1. PHYTASE ACTIVITY PRODUCED IN AND CO₂ EVOLVED FROM SOIL SAMPLES DURING 5 DAYS' INCUBATION IN PRESENCE OF ADDED ALFALFA MEAL

TABLE 1

Carbon dioxide produced and phytase activity developed by different fungi and a mixed population of microorganisms during 6 days' incubation of Clarion silt loam containing 2 per cent alfalfa meal

INOCULUM	CARBON DIOXIDE PRODUCED	PHYTASE ACTIVITY, AS PHYTATE P HYDROLYZED
	mgm.	mgm.
<i>Penicillium chrysogenum</i>	355	3.11
<i>Aspergillus niger</i>	440	1.74
<i>Cunninghamella blakesleana</i>	313	1.34
<i>Rhizopus nigricans</i>	139	0.10
<i>Actinomucor</i> sp.....	191	0.04
Mixture of above fungi (<i>A. niger</i> dominant)	456	1.56
Nonsterile soil.....	750	0.84

related increase in phytase activity. Because sterilization prior to inoculation would destroy any phytase originally present in the soil or added in the alfalfa meal, it may be concluded that the mixed culture of microorganisms that developed from the soil inoculum was the source of the phytase. It appears, therefore, that phytase activity in field soils can be accounted for on the basis of microbial metabolism therein. Phytase added as such in plant materials probably exists only temporarily in the soil.

Tables 1 and 2 show the CO₂ production and phytase activity associated with soil cultures of different fungi and bacteria, respectively. All the organisms tested

appeared to produce some phytase, although the amount was not so clearly related to CO_2 production as in the preceding experiment (fig. 1), in which a mixed population of soil microorganisms was supplied with different amounts of decomposable plant materials. Table 1 shows that three pure cultures and one mixed culture of fungi produced considerably less CO_2 and more phytase than did a mixed population of microorganisms derived from inoculation from a non-sterile soil. Since the phytase content of a soil at a given time probably represents the balance between the rates of synthesis and destruction, differences in the dependence of phytase activity on CO_2 production between organisms are not unexpected.

The production of phytase by *Arthrobacter helvolum* is worthy of particular mention, since this organism is one of Winogradsky's (10) "autochthonous" flora, the members of which are widely distributed, unresponsive to changes in en-

TABLE 2

*Carbon dioxide produced and phytase activity developed by different bacteria during incubation of Clarion silt loam with different plant materials**

INOCULUM	INCUBATION PERIOD	CARBON DIOXIDE PRODUCED	PHYTASE ACTIVITY, AS PHYTATE P HYDROLYZED
	days	mgm.	mgm.
1. None.....	18	5	-0.03
2. <i>Arthrobacter helvolum</i> †.....	18	30	0.14
3. <i>B. cereus</i>	10	55	0.15
4. <i>B. subtilis</i>	10	175	0.03
5. <i>Bacillus</i> sp. (contaminated last 5 days)	10	400	1.76

* For inoculum Nos. 1 and 2, 1 per cent corn stover added to soil; incubation at 31.7 per cent soil moisture; for Nos. 3, 4, and 5, 1 per cent alfalfa meal added to soil; incubation at 20.1 per cent soil moisture.

† Count at end of incubation, 10^9 organisms per gram.

vironment, and possessed of a low metabolic rate. This type of organism may continuously maintain a small amount of phytase in soil, even in absence of sufficient decomposable material to support the "zymogenous" flora.

PHYTASE ACTIVITY AT DIFFERENT PH VALUES

To investigate the phytase activity in soils previously maintained at different pH values, samples of Marion silt loam and of Shelby silt loam (C horizon) were adjusted to pH values of 5, 6, and 7. Samples of 200 gm. of soil were then treated with 1 gm. of sucrose and 0.5 gm. of nitrogen as NH_4NO_3 , moistened with 50 ml. of water, and incubated at 28°C . for 2 and 11 days before phytase activity was measured. Since the Shelby C horizon was extremely deficient in available phosphorus, the series of samples incubated 11 days received phosphorus as KH_2PO_4 in addition to the sugar and NH_4NO_3 ; the series incubated 2 days received no supplemental phosphorus.

Table 3 shows that the phytase activity in the soil increased as the pH de-

creased except in the samples of Shelby C horizon where no supplemental inorganic phosphorus was added. This effect of pH did not result from failure of the method to measure phytase activity at a constant pH value, since the reaction of the samples after addition of all reagents was constant to 0.03 pH unit. It appears, therefore, that the difference in phytase activity between pH values resulted from qualitative or quantitative differences in the microbial population. Since activities of fungi generally increase in relation to those of bacteria at low pH values, it may be speculated that the increase in phytase activity with decreasing pH resulted from changes in the balance of fungi and bacteria. Certain evidence in support of this possibility appears in table 1, which shows that several fungi produced less CO₂ and more phytase than did a mixed culture of organisms derived from nonsterile soil inoculum.

TABLE 3

Phytase activity developed by incubation of two soils at different pH values and for different lengths of time

SOIL TYPE	pH	PHYTASE ACTIVITY, AS PHYTATE P HYDROLYZED	
		Incubated 2 days	Incubated 11 days
		<i>mgm.</i>	<i>mgm.</i>
Marion silt loam	5	4.98	4.30
	6	1.88	2.65
	7	0.87	0.72
Shelby silt loam (C horizon)	5	0.07	4.89*
	6	1.10	2.68*
	7	0.58	0.88*

* Inorganic phosphorus was added to these samples before incubation.

PHYTASE ACTIVITY WITH CHANGES IN MOISTURE CONTENT AND TIME

Because of the unstable nature of enzymes, the effect of treatment of the soil samples before determination of phytase activity was investigated to see whether any significant effects were produced by different degrees of drying and different times of storage. Samples of three soils were treated with sugar and nitrogen, and were moistened and incubated to develop the phytase activity. Portions of these samples were then dried to varying degrees with a fan at room temperature, and the moisture content and phytase activity were determined. Samples of one soil were stored at constant moisture content for different lengths of time before determination of phytase activity.

Figure 2 shows that in all three soils the phytase activity decreased upon partial drying. Figure 3 shows that the phytase activity changed with time of storage before analysis. The change with time increased with the moisture content during storage. These results show that the phytase activity in a given soil does not remain at a constant level irrespective of the previous treatment. Apparently, phytase activity should be measured on the moist soil immediately after sampling and without previous drying. Storage of the soil sample at its original mois-

ture content for a time before analysis will probably have relatively less effect on the phytase activity in field samples than was found in the samples in figure 3 because of the presence of added energy material in the latter.

The effects of storage time shown in figure 3 can be accounted for on the basis of changes in microbial activity with time. The decrease in phytase activity upon partial drying may result from some effect of drying on the enzyme itself, from some change in the effect of soil on the enzyme, or from a combination of the two processes. No investigation was made of an independent effect of drying. It is known, however, that the activity of the enzyme is not destroyed by air-drying (6). Some evidence was obtained to support the view that deactivation of phytase by reaction with the soil increases as the soil moisture content decreases. An experiment was conducted on samples of Clarion silt loam treated with potas-

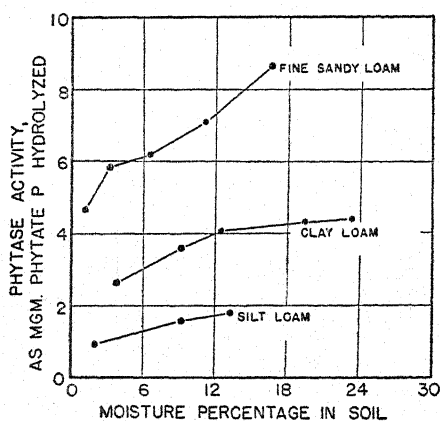


FIG. 2

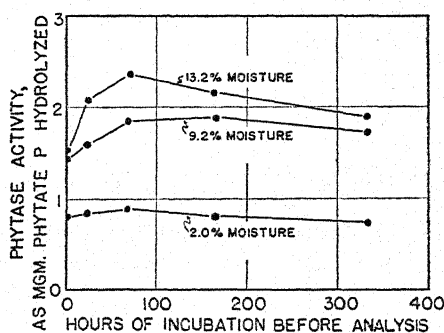


FIG. 3

FIG. 2. PHYTASE ACTIVITY IN SOIL SAMPLES AFTER DRYING TO DIFFERENT MOISTURE PERCENTAGES

FIG. 3. PHYTASE ACTIVITY IN SOIL SAMPLES AFTER DRYING TO DIFFERENT MOISTURE PERCENTAGES AND INCUBATION FOR DIFFERENT LENGTHS OF TIME BEFORE ANALYSIS

sium citrate and sodium phytate, as in the method for measuring phytase activity, but with an additional source of phytase in the form of a dilute suspension of phytase extract from bran (6). When the phytase was added after the other reagents, hydrolysis of the phytate was far greater if the enzyme reaction was allowed to proceed with only occasional shaking of the flasks than it was if the flasks were shaken continuously. Hydrolysis under the latter conditions was a little greater than it was when the enzyme was added first and the soil was partly dried under a fan at room temperature before addition of the other reagents, the flasks being shaken only occasionally during the reaction time. These results indicate that as the contact between soil and enzyme is increased, the extent of enzyme deactivation is likewise increased. Since contact between the enzyme and the solid phase of the soil should increase as the soil moisture content is reduced, the observed reduction of phytase activity in soils from partial drying may possibly be the result of increasing adsorption of the enzyme by the soil. This view is

in agreement with the observation of Ensminger and Giesekeing (3) that proteins are adsorbed by clays and the observation of Bower (1) that nuclease activity in a solution is reduced by the presence of bentonite.

DISCUSSION

It was found that soils contain phytase. When the native phytase was destroyed by steam-sterilization, phytase reappeared in the soil when a mixed culture of microorganisms or pure cultures of fungi or bacteria were allowed to develop. When the magnitude of a mixed population of microorganisms was varied by the supply of organic material added to the soil, the phytase activity developed was proportional to the amount of CO_2 evolved. Apparently, the occurrence of phytase in soils can be accounted for by microbial synthesis and the amount of phytase increases with the metabolic activity of the microbial population. The rate of hydrolysis of native soil phytin should thus increase with the metabolic activity of the microbial population in the soil if, at the levels present, phytase activity is important as a limiting factor.

It was found also that when phytase activity was developed in soils by incubation in the presence of energy material after prior adjustment of the soil reaction to pH 5, 6, and 7, the phytase activity increased as the pH became lower. This result would not be predicted from Bower's (1) finding that plant availability of phytate phosphorus added to soils is positively correlated with the pH value and percentage base saturation of the soil. Neither would it be predicted from the finding⁴ that the content of phytate phosphorus in soil increases as the pH becomes lower. Since the solubility of added phytate phosphorus is low (1, 5), however, and since the plant availability is probably correlated with the solubility (1), it appears that phytate solubility and not phytase activity may be the more important factor in controlling plant availability of added phytate phosphorus. The same reasoning applies to the soil phytate phosphorus.

Since phytase activity in soils reflects the metabolic activity of the microbial population, it is evident that the phytase activity found in a particular soil sample by the method proposed is not a constant characteristic of the soil. In addition to fluctuations due to microbial metabolism, the phytase activity found in the soil may be greatly modified by the treatment given the soil sample before analysis. Comparative results between samples may thus be obtained only where the preanalysis procedure is standardized. If the object is a measurement of the phytase activity in a particular soil at the time of sampling, it appears that the most reliable result will be obtained if the measurement is made immediately after sampling without preliminary drying or storage.

SUMMARY

Phytase activity was measured in soils by determining the inorganic phosphorus produced from added phytate phosphorus during 20 hours' incubation

⁴ Jackman, R. H. Mineralization of inositol-bound phosphorus in soil. 1949. [Unpublished doctor's thesis. Copy on file Iowa State College Library, Ames.]

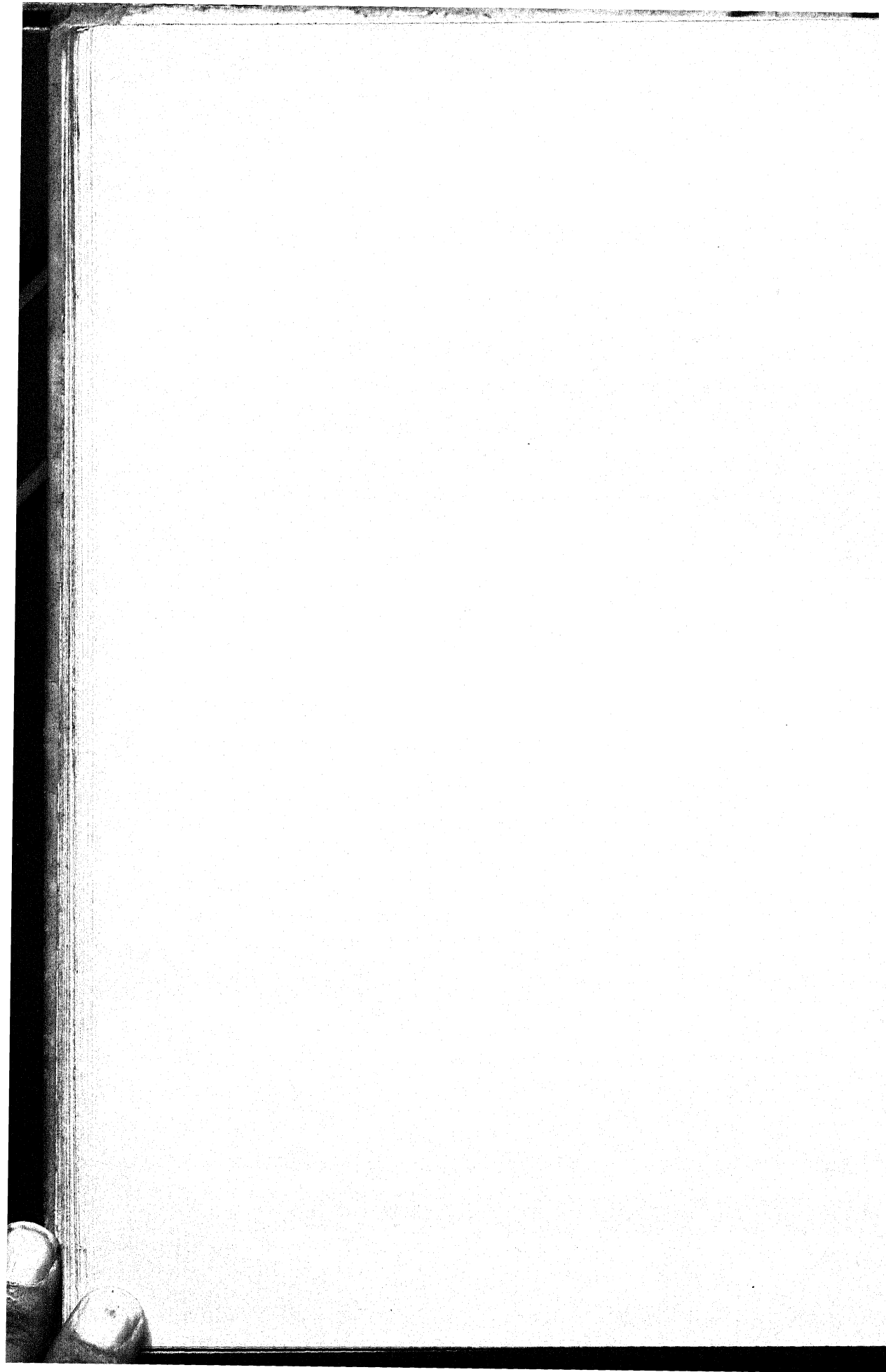
at 45° C. in the presence of citrate at pH 5. The activity was greater when the measurement was made on the moist soil as sampled than when the soil sample was partly dried at room temperature before analysis. Phytase activity also changed with time after sampling.

When soil treated with varying quantities of alfalfa meal was steam-sterilized to destroy the native phytase and microbial population, and then inoculated with a mixed soil flora, the amount of phytase activity produced was proportional to the amount of CO₂ evolved from the soil during incubation. When similar soil samples were inoculated with various pure cultures of bacteria or fungi, development of the organisms produced phytase activity in every case.

When soils treated with organic material were adjusted to pH 5, 6, and 7 and incubated to develop the microbial population, the phytase activity was found to be greatest at pH 5 and least at pH 7. Since in pure culture there was some indication that production of phytase by fungi was greater than that by bacteria, and since the proportion of fungi in the soil population generally increases with increasing acidity, the difference in phytase activity between pH values may have resulted from an increasing proportion of fungi in the population as the pH was decreased. If phytase activity in soils changes with pH in the manner found in this experiment, the limited plant availability of phytate phosphorus added to acid soils as compared with that added to neutral soils cannot be accounted for by a deficiency of phytase in the former. A decrease in phytase solubility with soil pH furnishes a more likely explanation.

REFERENCES

- (1) BOWER, C. A. 1949 Studies on the forms and availability of soil organic phosphorus. Iowa Agr. Exp. Sta. Res. Bul. 362.
- (2) DICKMAN, S. R., AND BRAY, R. H. 1940 Colorimetric determination of phosphate. *Indus. and Engin. Chem., Analyt. Ed.* 12: 665-668.
- (3) ENSMINGER, L. E., AND GIESEKING, J. E. 1942 Resistance of clay-adsorbed proteins to proteolytic hydrolysis. *Soil Sci.* 53: 205-209.
- (4) HOFF-JØRGENSEN, E., AND PORSDAL, V. 1947 On the phytase activity in rye flour and the phytate content of rye bread. *Akad. Tekn. Vidensk., Copenhagen, Trans.* 1947, No. 2.
- (5) JACKMAN, R. H., AND BLACK, C. A. 1951 Solubility of iron, aluminum, calcium, and magnesium inositol phosphates at different pH values. *Soil Sci.* 72: 179-186.
- (6) JACKMAN, R. H., AND BLACK, C. A. 1951 Hydrolysis of iron, aluminum, calcium, and magnesium inositol phosphates by phytase at different pH values. *Soil Sci.* 72: 261-266.
- (7) MICHAELIS, L., AND MENTON, M. L. 1913 Die Kinetik der Invertinwirkung. *Biochem. Ztschr.* 49: 333-369.
- (8) PEARSON, R. W., NORMAN, A. G., AND HO, C. 1942 Mineralization of the organic phosphorus of various compounds in soil. *Soil Sci. Soc. Amer. Proc.* (1941) 6: 168-175.
- (9) ROGERS, H. T., PEARSON, R. W., AND PIERRE, W. H. 1941 Absorption of organic phosphorus by corn and tomato plants and the mineralizing action of exoenzyme systems of growing roots. *Soil Sci. Soc. Amer. Proc.* (1940) 5: 285-291.
- (10) WINOGRADSKY, S. 1925 Études sur la microbiologie du sol. *Ann. Inst. Pasteur* 39: 299-354.



RESPONSE OF CROP PLANTS TO I AND Br

HARVEY P. NEWTON AND STEPHEN J. TOTH

New Jersey Agricultural Experiment Station¹

Received for publication July 26, 1951

A previous contribution from this laboratory dealt with the I content of New Jersey soils and plants (10). Although the research evidence indicates that I applications do not produce yield increases (2, 3, 4, 7, 8, 12, 13), some stimulation has been reported (9, 15). Information on the effect of Br on plant growth is very meager (3, 13). Lewis and Powers (8) found that Cl had an antagonistic effect upon I toxicity in corn. No information is available on similar antagonism between I and Br, and little is known about the residual effects of I applications.

The purposes of the present study were to determine whether tomatoes would respond to I or Br applications to the soils on which they were being grown; to determine the residual effects of such I applications, using buckwheat as a test crop; and to investigate I-Cl and I-Br relationships in plants.

EXPERIMENTAL METHODS

To study the response of tomatoes to I application, nine New Jersey soils varying from 0.0 to 12.1 ppm. in total I were selected (11). The soils were collected from virgin areas, brought into the laboratory, air-dried, and screened.

Uniform weights of the soils were placed in 2-gallon ceramic pots, limed to either pH 6.5 or 7.0 with CaCO_3 , and treated with a 10-10-10 fertilizer equivalent to 1 ton an acre. N was supplied either as NH_4NO_3 or KNO_3 , P as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, K either as KNO_3 or KCl , and I or B as the K salts. Mg, as the sulfate at the rate of 100 pounds MgO an acre, and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, MnSO_4 , and ZnSO_4 at 20 pounds an acre each were added to all soils except the Lakewood, on which each rate of application was reduced one half. In all cases, C. P. reagent salts were used. CaCO_3 and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ were applied in the dry state and the other salts in solution, and all were thoroughly mixed with the soil.

Specific treatments were in triplicate and consisted of: 1. Check, all K as KNO_3 ; 2. One pound I an acre, remainder K as KNO_3 ; 3. Ten pounds I an acre, remainder K as KNO_3 ; 4. Ten pounds I an acre, remainder K as KCl ; 5. Check, all K supplied as KCl (Sassafras sandy loam only).

The soils were seeded to Rutgers tomatoes September 9, 1949. The plants were thinned later to two a pot and grown at optimum moisture levels by periodic additions of water. They were harvested at the blossom stage December 15, 1949.

Buckwheat was seeded February 26, 1950, following a second fertilizer treatment at half the rates used in the initial I study. The plants were thinned to four a pot. They were harvested April 3.

For the Br studies, five soils were selected, fertilized, and limed as in the I

¹ Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, the State University of New Jersey, department of soils.

study and were treated with KBr at rates equivalent to 50 and 100 pounds Br an acre. All treatments were in triplicate. Pots were seeded to Rutgers tomatoes on June 28, and the plants were thinned to one a pot when 2 inches high. They were harvested August 24, 1950, in the prebloom stage.

In the study of I-Cl and I-Br relationships in plants, solution culture techniques (15) were employed. A standard nutrient solution of the following composition was used in all tests:

KH_2PO_4	0.0023 M	B as boric acid	0.25 ppm.
$(\text{NH}_4)_2\text{SO}_4$	0.0007 M	Mn as sulfate	0.25 ppm.
$\text{Ca}(\text{NO}_3)_2$	0.0045 M	Zn as sulfate	0.25 ppm.
MgSO_4	0.0023 M	Fe as sulfate	1.00 ppm.
K_2SO_4^2	0.0020 M		

The standard nutrient solution had a pH value of 4.5. All cultures were renewed twice weekly.

Rutgers tomatoes were used in studying I-Cl relationships. They were grown in solution cultures containing 0, 0.5, and 5 ppm. I, respectively, in presence and absence of chlorine. The I-Cl ratio was 1:15. Treatments were in duplicate. Seeds were placed in sand on October 21, 1949. Later, two uniform seedlings were selected and placed in 1-gallon solution jars. Plants were harvested on January 6, 1950, at the flowering stage and fractionated into leaflets, petioles, stems, and roots.

Similarly, I-Br relationships were investigated, the tomatoes being grown in solution cultures containing 0, 1, 5, 10, and 20 ppm. Br in presence and absence of I. Treatments were in triplicate. Seeds were placed in sand on March 24, 1950, and small seedlings were transplanted to 1-gallon solution culture jars on April 20. Br treatments were started on April 27. The plants were harvested on May 23.

Immediately after the harvest of each crop, the samples were oven-dried at approximately 70° C. in a forced draft air oven, weighed, ground in a small Wiley mill, and stored. The samples were again dried at 70° C. prior to analysis.

I was estimated by the chromic-sulfuric acid digestion method of Houston (6); Br by a modification of Hibbard's procedure (5); and Cl was titrated electrometrically according to the Piper method (11) and with the apparatus designed by Best (1).

RESULTS AND DISCUSSION

Response of tomatoes to I applications

No differences in germination of tomatoes were noted because of the I treatments. Seedlings growing on Lakewood sand, which received I at the 10-pound-an-acre rate, exhibited signs of poor growth. Toxicity symptoms were more pronounced when K was supplied as the chloride. Retardation of growth was observed initially on Copake loam with 10 pounds I when K was supplied as KCl, but at harvest time these differences had disappeared. No other visual differences were observed because of the treatments.

² The K_2SO_4 was varied as necessary to make allowance for the K supplied as KI, KCl, or KBr.

Yields of tomato tops were not increased with the 1-pound-an-acre rate of application of I. The 10-pound rate was toxic to plants growing on the Norton, Lakewood, Lawrenceville, and Washington soils (table 1). Yields were lower when K was supplied as the chloride. For example, when I was applied to the Lakewood soil at the 10-pound rate and K as the nitrate, the yield of dry matter was 11.8 gm. a pot, whereas when the K was supplied as the chloride, the yield was only 2.8 gm.

Cl toxicity was ruled out because the rate of application was equivalent to only 150 pounds Cl an acre, and it is known that 1500 ppm. Cl in solution culture does not affect tomatoes adversely. Why Cl applied in conjunction with I should increase toxicity is not clear.

TABLE 1
Dry weight yields and I and Cl content of tomato tops

I added* Form of K.....	DRY WEIGHT†					I CONTENT					Cl CONTENT				
	0	1	10	10	0	0	1	10	10	0	0	1	10	10	0
	KNO ₃	KNO ₃	KNO ₃	KCl	KCl	KNO ₃	KNO ₃	KNO ₃	KCl	KCl	KNO ₃	KNO ₃	KNO ₃	KCl	KCl
	gm.	gm.	gm.	gm.	gm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.
Lakewood sand.....	22.2	20.0	11.8	2.8	—	0.20	1.20	61.20	73.65	—	720	820	1,640	9,030	—
Copake loam....	29.8	29.2	27.4	28.8	—	0.30	0.85	8.90	11.65	—	820	820	920	13,200	—
Squires loam....	21.6	22.2	22.1	20.7	—	0.50	0.50	3.20	3.40	—	720	1,130	820	10,500	—
Washington loam.....	5.8	5.9	2.8	2.0	—	0.60	0.60	2.35	2.75	—	2,050	1,640	2,460	9,750	—
Hoosic stony loam.....	20.9	21.4	23.5	22.1	—	0.60	0.65	4.90	5.30	—	1,230	1,030	1,130	6,770	—
Sassafras sandy loam.....	30.6	30.4	31.2	31.0	32.0	0.65	0.50	11.70	77.90	0.50	600	620	590	11,420	13,000
Norton silt loam.....	26.2	23.0	19.6	15.8	—	0.80	0.80	1.25	1.70	—	3,290	3,180	3,280	6,050	—
Collington sandy loam.....	6.4	7.1	8.0	6.5	—	0.85	1.00	4.00	5.30	—	2,460	2,150	1,850	7,700	—
Lawrenceville silt loam.....	12.1	10.3	8.5	3.3	—	1.05	1.80	6.55	8.05	—	2,360	1,950	2,150	8,620	—

* In pounds per acre, as KI.

† Average yields of triplicate treatments.

The I content of tomato plants grown on the untreated soils varied considerably and ranged from 0.20 ppm. on the Lakewood to 1.05 ppm. on the Lawrenceville soil (table 1). Addition of I at the rate of 1 pound an acre generally increased the I content of the plants. No increases in I content were obtained with plants grown on the Squires, Washington, and Norton soils, but large increases resulted on the Lakewood, Copake, and Lawrenceville soils. Very slight effect was noted on the Hoosic soil. At the 10-pound rate of application of I, large increases in I content of tomato tops were noted on all soils. The highest I content, 61.2 ppm., occurred on the Lakewood and the lowest, 1.25 ppm., on the Norton soil.

When all K was supplied as the chloride, I uptake was increased. These results are in contrast to those of Lewis and Powers (8) with corn. Why the presence of Cl should increase I uptake by tomatoes is not clear.

Whether Cl uptake is affected by I applications cannot be answered. The Cl

content of tomatoes varied with the nature of the soils, and ranged from 600 to 3,290 ppm. on the no-I treatments when K was supplied as KNO_3 (table 1). Addition of 150 pounds Cl an acre as KCl markedly increased the Cl content of the plants.

Variations existed in the I content of fractions of tomato plants grown on Sassafras sandy loam at different levels of I (table 2). When I was not supplied, the I content of the fractions decreased in the following order: roots, upper leaves, lower leaves, lower stems, and upper stems. When I was applied at the 10-pound-an-acre rate in conjunction with K supplied as the chloride, the order of decreasing I content was: lower leaves, lower stems, roots, upper leaves, and upper stems. When comparison is made of the I content of the various fractions of tomato plants grown at the I applications of 10 pounds an acre and K supplied as the chloride or nitrate, the relative distribution of I was found to be the same,

TABLE 2

Distribution of I and Cl in various fractions of tomatoes grown on Sassafras sandy loam

TREATMENT		I CONTENT					Cl CONTENT				
I added*	Form of K	Upper Leaves	Lower Leaves	Upper Stems	Lower Stems	Roots	Upper Leaves	Lower Leaves	Upper Stems	Lower Stems	Roots
lb./A.		ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.
0	KNO_3	0.95	0.70	0.45	0.50	3.25	820	510	1,130	410	310
1	KNO_3	0.65	0.90	0.35	0.25	1.55	925	615	1,330	310	410
10	KNO_3	14.40	90.00	4.55	14.80	23.00	720	410	1,230	410	310
10	KCl	24.40	153.40	14.40	48.70	30.60	6,360	10,260	14,990	13,240	7,290
0	KCl	1.00	0.75	0.60	0.15	1.30	6,980	13,750	15,290	13,750	6,670

* I added as KI.

but the actual amount of I found in the fractions was higher when K was supplied as the chloride.

Residual effects of I applications

Buckwheat yields were not increased by I applications except on the Norton soil, and these may be considered to be well within experimental error (table 3). It will be recalled that I at all levels on this soil initially were toxic to tomatoes. Buckwheat on the Lakewood and Lawrenceville soils exhibited toxicity similar to that noted with tomatoes. Buckwheat yields were reduced on the Hoosic, although tomatoes had not exhibited symptoms of toxicity when previously grown on this soil. Yields of buckwheat from Copake, Collington, Squires, and Sassafras soils were not significantly affected by previous I treatments. In most cases, yield decreases from I applications at the 10-pound rate, with K added as KCl, were more pronounced than when K was added as KNO_3 . Cl seemed to increase rather than counteract I toxicity.

Residual effects from the initial I treatment at the rate of 1 pound an acre were still reflected in the I content of buckwheat grown on all except the Norton, Copake, and Washington soils (table 3). On the Sassafras soil, the I content increased from 0.85 ppm. to 1.00 and 2.85 ppm. as the initial I application was

increased from 0 to 1 and 10 pounds an acre. The residual effect from the 10-pound application was more pronounced than that from the 1-pound rate and also was greater on the Sassafras, Collington, Squires, Copake, and Lakewood

TABLE 3
Dry weight yields and I and Cl content of buckwheat grown as residual crop

I added* Form of K.....	DRY WEIGHT†					I CONTENT					Cl CONTENT				
	0	1	10	10	0	0	1	10	10	0	0	1	10	10	10
	KNO ₃	KNO ₃	KNO ₃	KCl	KCl	KNO ₃	KNO ₃	KNO ₃	KCl	KCl	KNO ₃	KNO ₃	KNO ₃	KNO ₃	KCl
	gm.	gm.	gm.	gm.	gm.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Lakewood sand.....	4.1	3.9	3.4	2.7	—	1.30	2.10	12.35	10.30	—	1,330	1,330	1,330	4,920	—
Leaves.....						1.05	1.00	9.45	11.55	—	1,950	1,540	1,740	8,930	—
Stems.....						0.75	0.80	6.75	9.45	—	820	720	820	11,300	—
Copake loam.....	3.8	3.5	3.6	3.4	—	0.65	1.05	2.40	6.00	—	1,020	1,130	1,230	9,240	—
Squires loam.....	3.2	3.0	2.8	2.8	—	0.80	0.80	1.50	1.20	—	1,130	1,440	1,540	6,460	—
Washington loam.....	2.5	1.4	2.3	2.1	—	0.95	0.65	6.75	9.45	—	820	1,030	1,130	6,460	—
Hoosic stony loam.....	3.0	2.5	2.3	1.7	—	0.85	1.00	2.85	3.85	0.90	920	1,130	1,030	9,450	7,700
Sassafras sandy loam.....	3.2	3.0	2.9	3.1	3.1†	0.65	0.70	1.55	1.40	—	1,850	2,050	2,050	4,720	—
Norton silt loam.....	3.3	3.5	3.6	2.8	—	1.05	1.25	8.75	11.35	—	1,540	1,740	1,740	7,080	—
Collington sandy loam.....	2.1	2.2	1.8	1.8	—	1.00	1.50	3.40	3.40	—	1,640	1,330	1,640	3,800	—
Lawrenceville silt loam.....	2.8	2.1	1.7	1.5	—										

* Pounds an acre, as KI, to tomatoes harvested previously.

† Average yields from triplicate pots.

‡ Average 2 pots.

TABLE 4
Dry weight yield of Rutgers tomatoes as affected by Br applications

Br added*.....	DRY WEIGHTS†		
	0	50	100
	gm.	gm.	gm.
Annandale loam.....	12.4	12.0	11.5
Norton silt loam.....	5.9	5.0	5.2
Sassafras sandy loam.....	9.9	10.3	10.5
Squires loam.....	9.4	10.1	10.7
Collington loam.....	9.6	10.4	8.7

* Pounds an acre, as KBr.

† Average yield of triplicate pots.

than on the Norton, Lawrenceville, and Washington soils. The effect of Cl on the I uptake was still reflected in the second crop on all soils. The Cl content of the buckwheat was unaffected by the previous I applications (table 3).

Response of tomatoes to Br

No visual differences were noted in tomatoes grown on the five soils following application of Br at rates of 50 and 100 pounds an acre. Slight increases in yield

were noted on the Sassafras and Squires soils (table 4). A slight increase was also noted on the Collington soil at the rate of 50 pounds an acre. The increases were not significant. A slight reduction of yield was noted on both the Annandale and Norton soils, but this was probably not significant.

TABLE 5

Dry weight yields and I, Cl, and Br content of leaflets, stems, and roots of tomatoes

TREATMENT		DRY WEIGHTS*			I CONTENT			Cl CONTENT			Br CONTENT		
I	Br	Tops	Roots	Total	Leaflets	Stems	Roots	Leaflets	Stems	Roots	Leaflets	Stems	Roots
ppm.	ppm.	gm.	gm.	gm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.
0	0	15.7	3.4	19.1	1.55	0.90	3.80	410	410	410	40	—	—
0	0	12.9	3.1	16.0	533.90	603.00	275.10	410	410	510	<4	—	—
2	1	14.9	3.0	17.9	651.70	575.50	313.20	720	620	510	<4	—	—
2	5	13.7	2.9	16.6	717.30	433.80	275.10	820	1030	620	<4	—	—
2	10	16.1	3.4	19.5	647.50	581.90	317.40	1440	2050	1750	<4	—	—
2	20	12.4	3.1	15.5	760.70	558.60	323.75	2050	3490	2050	<4	—	—
0	1	11.8	2.6	14.4	2.70	0.40	5.40	615	720	620	1440	—	—
0	5	16.6	2.8	19.4	2.10	1.60	4.75	1030	1540	1030	850	—	—
0	10	15.1	3.3	18.4	2.05	1.25	3.35	1540	2670	1440	1450	—	—
0	20	18.8	4.1	22.9	1.80	1.25	2.40	2670	5130	2460	2825	6320	2100

* Average of triplicate pots.

TABLE 6

Dry weight yields and I and Cl contents of leaves, petioles, stems, and roots of tomatoes

TREATMENT		DRY WEIGHTS*			I CONTENT				Cl CONTENT			
I	Cl	Tops	Roots	Total	Leave	Petioles	Stems	Roots	Leaves	Petioles	Stems	Roots
ppm.	ppm.	gm.	gm.	gm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.
0	0	17.0	1.7	18.7	2.80	2.75	1.50	10.60	720	920	510	310
0	7.5	22.0	1.9	23.9	2.95	2.40	2.25	6.40	2,050	6,880	7,800	3,800
0	75.0	21.6	2.3	23.9	3.55	6.15	2.40	7.50	3,900	14,880	16,620	8,620
0.5	0	16.4	1.6	18.0	255.20	302.00	216.00	380.00	510	720	510	510
5.0	0	9.2	1.5	10.7	744.80	1,523.50	1,555.00	603.00	920	1,640	820	1,130
0.5	7.5	18.0	2.0	20.0	338.00	281.20	214.00	338.00	1,330	3,900	4,310	2,770
5.0	75.0	6.3	0.8	7.1	952.20	2,190.00	1,785.00	687.00	4,510	14,370	—	5,390

* Average yield of duplicate pots.

I-Cl and I-Br relationships in tomatoes

Observations made on tomatoes grown in solution cultures at varying I and Cl levels showed that 5 ppm. I produced severe toxicity effects 12 days after the treatments were started. The leaves were mottled, lighter green areas appearing between the veins, while the areas immediately around the veins remained a healthy dark green. Some leaves showed a few necrotic spots along the edges and tips, while others were slightly curled along the edges. The presence of Cl in the nutrient solution augmented these symptoms. Two parts per million I produced

only a slight mottling, whereas 0.5 ppm. had no visible effect. Plants that received 7.5 or 75 ppm. Cl in absence of I appeared to grow vigorously.

Cl at levels of 7.5 and 75 ppm. stimulated growth in absence of I. Some stimulation was also observed at the 7.5 ppm. Cl and 0.5 ppm. I levels, whereas 2 ppm. I proved somewhat toxic, and the 5 ppm. I markedly reduced growth (tables 5 and 6). In the latter case the toxicity was increased by the presence of 75 ppm. Cl.

Both the I and Cl contents of the plant fractions increased directly with the levels of these elements in solution (table 6). Generally, the I contents of the various plant fractions were increased by the addition of Cl. For example, the leaf portions of the plants receiving 5 ppm. I and no Cl, contained 744.8 ppm. I, whereas when Cl was present to the extent of 75 ppm., the I content was 952.2 ppm. The effects of I on Cl uptake were variable.

Br additions up to 20 ppm. did not affect the growth of the plant (table 5). In a manner similar to I, the Br content of tomato leaflets generally increased as the Br level in the nutrient solution was raised. Increasing Br levels in the substrate did not affect the I content of tomatoes. Although Cl-Br relationships were not a part of this study, the data show that an increase in Br in the substrate tended to increase Cl uptake.

SUMMARY

Applications of KI were made to nine New Jersey soils, and tomatoes were used to test the effect of the added I. Residual effects of the I additions were studied on buckwheat as a test crop. A preliminary test was made of the effect of Br additions. I-Cl and I-Br relationships in tomatoes were studied by use of solution-culture procedures.

Yield responses were not obtained with tomatoes on any of these soils when I was applied at rates of 1 and 10 pounds an acre. I at the 1-pound rate had no effect on the growth of tomatoes on the soils, but at the 10-pound rate it was toxic to tomatoes on the Norton, Lawrenceville, Washington, and Lakewood soils.

Addition of Cl as KCl tended to increase toxicity symptoms of I in soil cultures and also to increase I uptake by both tomatoes and buckwheat.

Residual effects of the initial I applications were observed on the yield and I content of buckwheat from several soils.

Yield responses from Br applications at rates of 50 and 100 pounds an acre were not obtained on five typical New Jersey soils.

I-Cl antagonism was not observed in tomatoes in either solution tests or soil tests.

I uptake was increased by addition of Cl, but no effect of I on Cl uptake was observed.

I-Br antagonism was not observed in solution cultures, although Br seemed to increase Cl uptake.

The Br content of leaflets of tomatoes grown in the tests ranged from less than 4 ppm. to 2,825 ppm. depending on the amount of Br present in the nutrient solution.

REFERENCES

- (1) BEST, R. J. 1929 A rapid electrometric method for determining the chloride content of soils. *Jour. Agr. Sci.* 19: 533-40.
- (2) Chilean Iodine Educational Bureau Publication 1950 Iodine and Plant Life. Stone House Bishops Gate, London.
- (3) Chilean Nitrate Educational Bureau, Inc. 1948 Bibliography of the literature on minor elements. New York.
- (4) GAUS, W., AND GREISBACH, R. 1928 Jodfrage und Landwirtschaft. *Ztschr. Pflanzenernähr., Düngung, Bodenk.* (A) 13: 320-425.
- (5) HIBBARD, P. L. 1926 The chromic acid method for estimation of small amounts of bromine. *Indus. and Engin. Chem.* 18: 57-60.
- (6) HOUSTON, F. G. 1950 Microdetermination of iodine in plant material. *Analyt. Chem.* 22: 493.
- (7) LEWIS, J. C., AND POWERS, W. L. 1941 Iodine in relation to plant nutrition. *Jour. Agr. Res.* 63: 623-37.
- (8) LEWIS, J. C., AND POWERS, W. L. 1941 Antagonistic action of chlorides on the toxicity of iodides to corn. *Plant Physiol.* 16: 393-98.
- (9) MAZE, P. 1919 Recherche d'une solution purement minérale capable d'assurer l'évolution complète du maïs cultivé à l'abri des microbes. *Ann. Inst. Pasteur* 33: 139-73.
- (10) NEWTON, H. P., AND TOTH, S. J. 1951 Iodine content of some soils and plants of New Jersey. *Soil Sci.* 71: 175-179.
- (11) PIPER, C. S. 1947 Soil and Plant Analysis. Interscience Publishers Inc., New York.
- (12) SCHARRER, K., AND SCHROPP, W. 1931 Untersuchungen über den Einfluss steigender Gaben von Jodid, Jodat, und Perjodation auf die Keimung und erste Jugendentwicklung einiger Kulturpflanzen. *Biochem. Ztschr.* 236: 187-204.
- (13) SCHARRER, K. 1941 Biochemie der Spurenelemente. Paul Parey, Berlin. Photolithoprint Reproduction, Edwards Brothers, Inc., Ann Arbor, Michigan.
- (14) SHIVE, J. W., AND ROBBINS, W. R. 1951 Methods of growing plants in solution and sand cultures. *N. J. Agr. Exp. Sta. Bul.* 636.
- (15) STOKLASA, J. 1924 The physiological function of iodine in the sugar-beet organism. *Compt. Rend. Acad. Sci. [Paris]* 178: 120-22.

THE ASPERGILLUS NIGER METHOD FOR DETERMINING COPPER IN SOILS

MARJORIE WELSH DOLE¹

Battelle Memorial Institute, Columbus, Ohio

Received for publication August 2, 1951

The recent recognition of copper deficiency in plants and animals has stimulated research on the availability of this element in soils. The usual laboratory analyses involving soil extracts may give little information about the copper available to the plant. Of particular interest, therefore, is the *Aspergillus niger* method, a bioassay based on the requirement of the fungus for copper to form pigment. First developed by Mulder (3, 4), the method was later studied by Acock (1) and Nicholas (5, 6, 7, 8). The assay is more rapid and less variable than plant tests of the Neubauer type. Its technique is simple. Soils can be assayed directly without extraction or measures to eliminate interfering ions. Most important, on soils low in copper, it gives a more accurate estimation of availability than do chemical or spectrographic analyses. The nutritional requirements of *A. niger* have been studied by Steinberg (9, 10, 11, 12).

It was the purpose of these studies to confirm and extend the bioassay method as it has been employed by others, and to evaluate its use for various United States soil types. As the work progressed, various modifications in the techniques described by others were adopted for convenience and efficiency. The final section of this paper is devoted to recommended procedures based on the experiences in the Battelle laboratory.

ASPERGILLUS NIGER CULTURES

The quantitative relationship between copper and pigmentation in *Aspergillus* and certain other organisms varies not only with the species, but also with the strain. Most strains of *A. niger* do not respond well to traces of copper. For these studies, several strains of the fungus² were compared for sensitivity to copper. The (M)FS strain was selected among these as having the best range of sensitivity. Without added copper, it forms a nonsporulating white mycelium on Mulder's medium after 5 days' incubation at 30°C. With increased increments of copper, coloration increases in intensity from shades of tan through brown. At 1 γ of copper, maximum sporulation and a very dark brown color result.

Stock cultures maintained on potato-dextrose agar slants may occasionally be subject to natural variation with modified sensitivity to copper. Figure 1 shows some of the "wild" variants which are likely to appear from time to time.

¹ The author gratefully acknowledges the advice and criticism given during the course of these studies by C. B. Harston and the staff of the Division of Agricultural Research. This research was made possible by the financial support of Anaconda Copper Mining Company, Kennecott Copper Corporation, and Phelps Dodge Corporation.

² Obtained through the courtesy of C. B. Harston, extension soil specialist, Washington Agricultural Experiment Station, Pullman.

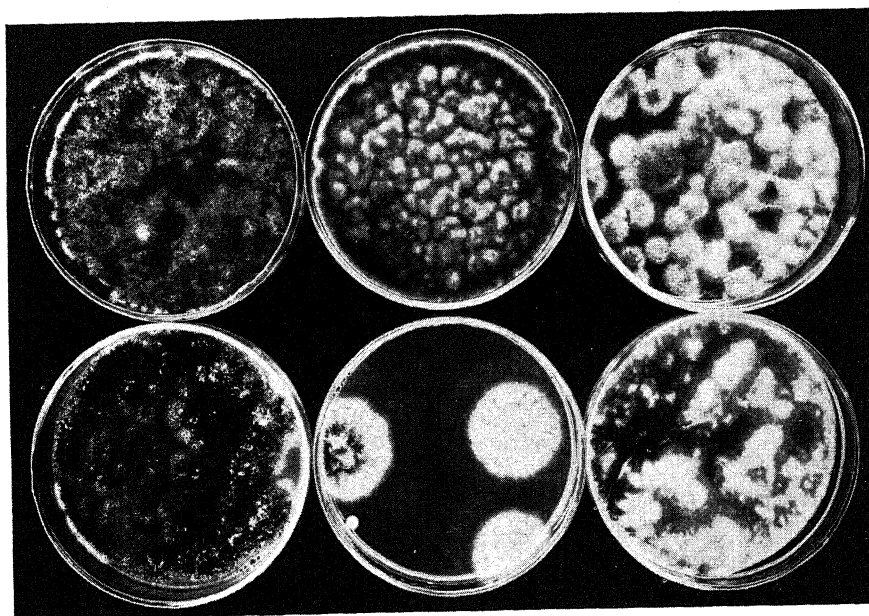


FIG. 1. SUBSTRAIN DIFFERENCES ARISING FROM NATURAL VARIATION OF *Aspergillus niger*
 Top left: original strain; top center: current strain; others: genetic aberrations

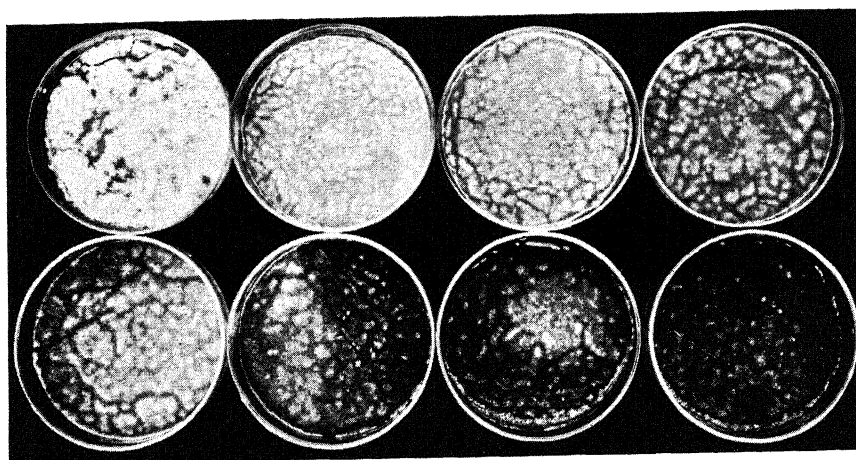


FIG. 2. COPPER STANDARDS OF THE *Aspergillus niger* ASSAY

Top row, left to right: 0, 0.1, 0.2, 0.3 γ copper; bottom row, left to right: 0.4, 0.6, 0.8, 1.0 γ copper

It was recently observed, however, that stocks maintained in a vegetative state in soil varied less than potato-dextrose cultures. This method of preservation of cultures as well as others has been described in detail by Foster (2).

REMOVAL OF HEAVY-METAL CONTAMINANTS

Contamination of media with traces of copper and other heavy metals may be reduced to a minimum by eliminating, so far as possible, all forms of copper

from the laboratory, carefully cleaning and rinsing pyrex glassware, double distilling all water through pyrex, and purifying the basal medium.

Media must be purified even when C.P. reagents are used. Five general methods will accomplish this: (a) purification of reagents by recrystallization and precipitation, (b) electrolysis, (c) formation of chelate complexes, (d) adsorption, and (e) precipitation.

The first two methods were not considered in this study, since purification is exacting and time-consuming, and the expense of electrolysis is probably prohibitive in most laboratories. Chelation with oxine and carbamate was tried, but it was difficult to remove all traces of these phytotoxic reagents. Insufficient copper was removed from the medium by Steinberg's calcium carbonate treatment (10) to permit a very sensitive assay. In our experience, the only method that removed sufficient copper from the basal medium, without adversely affecting growth and color development, was precipitation of the heavy metals as sulfides with subsequent adsorption on charcoal. This method, which has been described by Mulder (3), was also the simplest and least time-consuming.

An additional purification technique is by use of the organism itself to remove heavy-metal traces. This method is probably not practical for media purification, because of the undesirable metabolic products formed during growth. It was adapted in our laboratory, however, for purifying inert materials. By growing successive cultures of *A. niger* on sand and Amberlite, an organic resin, copper traces could be removed more completely than by acid-leaching.

Another source of contamination has been attributed to the spore inoculum. Steinberg (10), with alkaline solutions, extracted iron, manganese, and copper stored in spores. Acock (1) recommended use of brown spores from copper-deficient cultures for inoculation because of accumulations of copper in the darker spores. He found that markedly lighter cultures were obtained with brown spores than with black spore suspensions prepared in the same way. Only slightly darker cultures result when medium is inoculated with dark spores of the M(FS) strain. Because copper contamination is additive, however, the precaution of inoculating with pale tan spores was routinely exercised.

INTERPRETATION OF COPPER CONCENTRATION FROM ASPERGILLUS CULTURES

Three methods of determining the response of *Aspergillus* cultures to copper were evaluated: spore color, amount of sporulation, and mycelial weight.

A range of standard copper solutions containing 0–2.0 γ was added to 9-cm. pyrex petri dishes. Three replications were made for each increment of copper. Fifteen milliliters of preinoculated media were added and the cultures incubated. Spore colors were interpreted in terms of a numerical code shown at the bottom of table 1. Sporulation was recorded on a five-point scale (0 = none; 5 = maximum sporulation). The mats were dried to constant weight at 70°C. and the weights recorded in grams. Table 1, in which replications were averaged, shows that the best reflection of copper concentration with this volume of media is in spore color.

The sensitivity of spore color response was confirmed in later experiments, but the accuracy was variable. This may be due to different batches of media, the

amount and copper content of the spore inoculum, and natural variation in the stock strain of the fungus. Under optimal conditions, the accuracy is ± 0.01 in the 0–0.1 γ range, ± 0.025 in the 0.1–0.5 γ range, and ± 0.05 in the 0.5–1.0 γ range. The reliability of color differences has almost always been dependable for standard cultures containing 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0 γ of copper. Figure 2 illustrates typical growth responses to these levels of the element.

For routine assays of soils, direct readings of concentration are made by comparison of spore color with that of standard cultures. In the experimental studies with the fungus, on the other hand, the numerical scale was used to record spore color to show treatment differences. Because of the variables previously mentioned, these color values were regarded as only relative, and data from different experiments were never pooled.

TABLE 1

Comparison of spore color, amount of sporulation, and mycelial weight of Aspergillus cultures in response to copper

COPPER	SPORE COLOR*	AMOUNT OF SPORULATION†	MYCELIAL WEIGHT
γ			gm.
0	1	0.5	0.28
0.1	2	1	0.33
0.2	4	3	0.35
0.3	4.5	3	0.38
0.4	5	3	0.34
0.5	5.5	3	0.34
1.0	6	5	0.34
2.0	6	5	0.34

* Color code:

1 2 3 4 5 6 7
 White ←———— Tan —————→ ←———— Brown —————→ Dark Brown

† Sporulation code: 0 = none; 5 = maximum.

INFLUENCE OF PHYSICAL FACTORS

The effects of depth and surface area of the substrate on copper uptake were studied in a series of experiments. Depth was varied by volume changes and surface area by use of three sizes of petri dishes: large (14 by 2 cm.), medium (9 by 2 cm.), and small (5 by 1.5 cm.).

In the first experiment, volume alone was varied to find the effect of this factor on the quantitative expression of spore color and mycelial weight. For each volume of preinoculated medium added to 9-cm. petri dishes, a range of copper levels between 0 and 2 γ was prepared with two or three replications for each concentration. Results were expressed in terms of spore color and mycelial weight. Figure 3 shows the relationship between these two variables. Numerical values for spore color were recorded on a semilogarithmic grid to allow straight-line comparisons between volumes. Note that as volume increases, greater differences in mycelial weight result between different copper levels; at the same

time, the range of color responses remains about the same for all volumes. However, cultures with greater volumes do tend to have some color development in absence of added copper; whereas distinctly white mycelia are usually the rule with the smaller amounts of media. Apparently, estimations of copper in the 0-1.0 γ range can best be made by spore color when the depth is minimal and by mycelial weights when greater volumes of media are used.

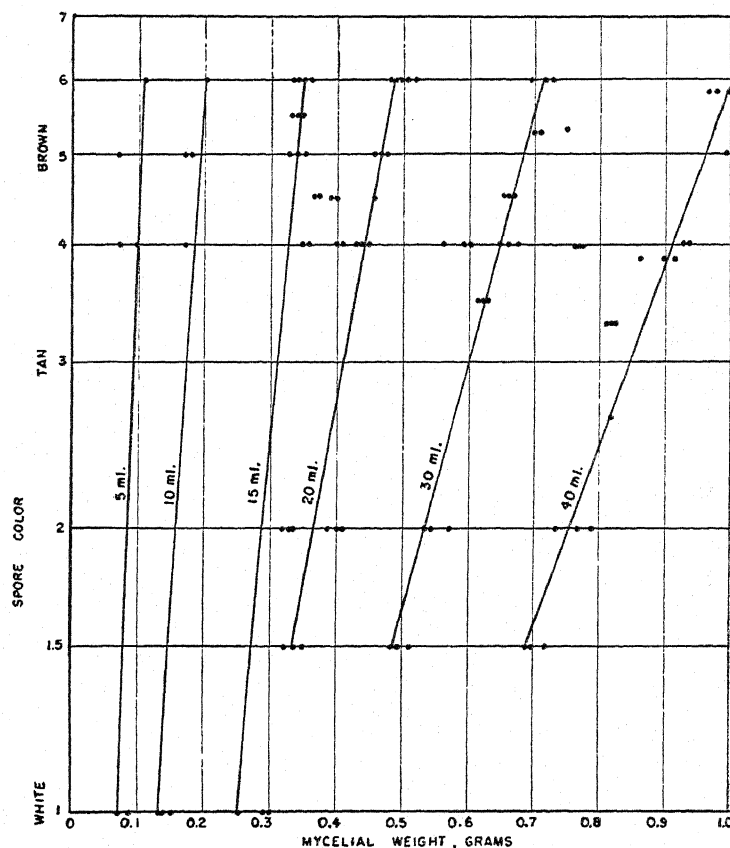


FIG. 3. RELATIONSHIP BETWEEN SPORE COLOR AND MYCELIAL WEIGHT OF *ASPERGILLUS* CULTURES IN RESPONSE TO COPPER AT VARIOUS VOLUMES OF MEDIA

In another experiment, the effects of depth and surface area on spore color alone were considered. The medium was inoculated and dispensed with the following volumes: small dishes, 5 and 10 ml.; medium dishes, 10, 15, 20, 30, and 40 ml.; large dishes, 30 and 40 ml. A series of aliquots containing 0 to 1.0 γ of copper were added to each volume. After incubation, colors were recorded according to the numerical scale previously described. The results are shown in figure 4. In medium dishes, the color responses with increasing copper dosage are similar for the several volumes of medium. In comparison, small cultures have a lower threshold for dark color development, and the larger cultures show only small

color differences in the 0-0.5 γ range. A statistical analysis of the color differences resulting from the four volumes in the medium dishes showed that depth of medium had a significant influence on spore color development and that a depth of 5 mm. (30 ml.), was optimal. These differences may be misleading, however. Note that response to copper was interpretable from any of the four volumes and there is probably no objection to use of minimal volumes of media for economy.

It was hypothesized that the color reactions of the small and large cultures might indicate that they possessed a greater accuracy in the 0-0.1 γ and the 0.5-1.0 γ range respectively. This is evidently not the case, however, since further

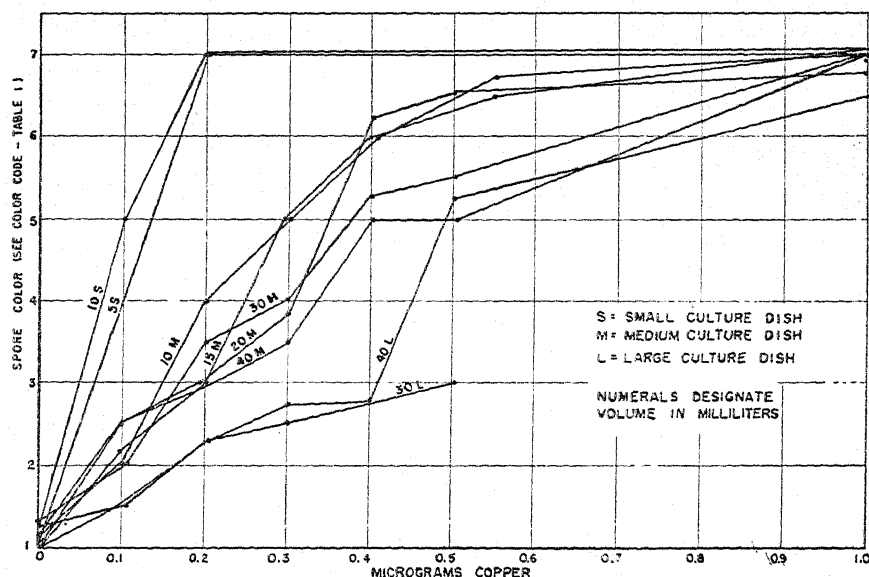


FIG. 4. EFFECTS OF DEPTH AND SURFACE AREA ON SPORE COLOR OF *Aspergillus* CULTURES

observations indicated that the accuracy was not increased by varying the surface area.

COMPARISON OF THE BIOASSAY WITH OTHER METHODS OF ANALYSIS

Mulder (3, 4) and Acock (1) demonstrated that the *A. niger* method agrees very well with crop responses to soils of varying fertility. Acock also showed that bioassay results were in better agreement with field evidence than the spectrographic and chemical data obtained from HCl extracts of Australian soils. Comparisons of these three methods with crop responses are in progress on United States soil types. Preliminary data have been collected on some random soil types to note the degree of agreement between results of the bioassay and of spectrophotometric and spectrographic analyses of Morgan's solution leachates. From the data assembled, part of which are shown in table 2, there is no apparent relationship between the results of the three methods.

COPPER UPTAKE BY SPORES

The differences observed between the bioassay and other methods led to some preliminary studies on the mechanism by which *A. niger* obtains copper. The strain of *Aspergillus* used is acid-producing. Acidity of the medium may drop from pH 6 to pH 4 or even pH 3 during the first 2 days of incubation. Cultures become alkaline during the subsequent 3 days. No pH differences in the substrate occur between copper levels. The hypothesis is that the acid production makes adsorbed as well as ionic copper available to the fungus.

To determine the availability of adsorbed copper, Amberlite Grade XE-66-B,³ a synthetic ion-exchange resin, was used. The resin was leached with 1:4 HCl and, after thorough rinsing with double distilled water, various concentrations

TABLE 2

Comparison of chemical and spectrographic assays of available copper in soils with the bioassay

SOIL NO.	SOIL TYPE	ESTIMATED AVAILABLE COPPER		
		Chemical Analysis	Spectrographic Analysis	Bioassay
		<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>
—	Muck	0.5	0.2	8.0
147	Sandy loam	0.2	0.2	>10.0
1048	Sandy clay loam	0.4	0.2	5.0
1147	Sandy	0.5	0.2	4.0
1247	Plummer fine sandy loam	0.4	0.2	4.0
1748	Silt loam	0.2	0.2	2.5
5948	Clay	—	6.3	1.75
8048	Felida silty loam	—	2.5	3.25
8948	Sauvie silty loam	—	8.8	>10.0
9548	Sauvie clay loam	—	18.8	>10.0
9848	Columbia fine sandy loam	—	12.5	>10.0
11448	Rubicon loamy fine sand	—	3.8	4.0

of copper were quantitatively adsorbed on the surface. The effects of both direct and indirect contact between this copper source and the fungus were measured. To determine the effect of direct contact, 30 ml. of preinoculated medium was added to duplicate culture dishes containing various concentrations of copper adsorbed on 0.25 gm. Amberlite. This amount of medium was selected since it provides the shallowness desired for direct contact between mycelium and copper source and also has sufficient volume to minimize the slight toxic effect of Amberlite on growth of *A. niger*. Adsorption of the copper on the resin was accomplished by adding the copper in solution to the Amberlite and allowing contact for 24 hours. At the end of this period, the supernatant liquid was found to be completely free of the element, and it was assumed that all of the added copper was exchanged with H ions on the resin surface. The spore colors that developed after direct contact between adsorbed copper and the fungus were averaged and are recorded in table 3.

³ Obtained through the courtesy of The Rohm and Haas Company, Philadelphia.

Acid-leached Amberlite possesses sufficient copper available to the fungus to cause the development of brown (code 5) spores. It is evident from table 3, however, that when added copper was adsorbed on the resin, and direct contact between it and the mycelium was allowed, an even darker spore color (code 7) resulted. This indicates that the adsorbed copper is taken up by the fungus.

The effects of indirect contact between *A. niger* and adsorbed copper were determined by separating the copper source from the fungus by a semipermeable membrane. Cellophane, which is impermeable to colloidal clay but porous enough

TABLE 3
Availability of adsorbed copper for *A. niger* spores

COPPER ADDED	SPORE COLOR*					
	Direct Contact†		Indirect Contact†			
	Ionic Copper	Adsorbed Copper	Ionic Copper		Adsorbed Copper	
			Series 1	Series 11	Series 1‡	Series 11‡
γ						
0	1	5	1	1	1	1
0.2	2	5	3	4	—	—
0.4	4	—	4.5	5.5	—	—
0.6	6	—	5	5.8	—	—
0.8	7	—	6	6	—	—
1.0	7	—	6	6	—	—
2.0	7	7	5	7	2	4
5.0	—	—	7	7	—	—
10.0	—	—	7	7	—	—
20.0	7	7	7	7	5	7

* Color code:

1 2 3 4 5 6 7
White ←———— Tan —————→ ←———— Brown —————→ Dark Brown

† Direct contact: *A. niger* mycelium in contact with copper source in petri dish cultures; indirect contact: *A. niger* and copper source in paired cell cultures.

‡ Series 1: copper separated from spores by semipermeable membrane; series 11: copper and spores on same side of semipermeable membrane.

to allow passage of ions, was used for this purpose. Paired glass cells (fig. 5) each 3 cm. long were prepared from 3½-cm. Pyrex glass tubing. A square of cellophane was placed between the ground glass apertures of two cells and the pair joined with a rubber band. Each cell was constructed with an 8-mm. inlet for addition of medium and spores, and also to allow air exchange. Cotton plugs were inserted in the inlets before sterilization. Fifteen milliliters of medium was added aseptically to each cell, and 0.5 ml. of a spore suspension was added to one cell of each pair.

The average spore colors that developed in duplicate paired cells after indirect contact with adsorbed copper are compared in table 3 with the colors that resulted when ionic copper was added to the system. Between 0 and 1.0 γ, separa-

tion of the copper source from the *Aspergillus* culture by the semipermeable membrane did not allow maximum availability of ionic copper. At concentrations above 1.0 γ , sufficient copper was evidently present for maximum coloration, even though the rate of diffusion was probably slowed by presence of the cellophane. Adsorption of the copper on Amberlite apparently also retarded the rate of copper uptake by the spores. Note that in Series II, where adsorbed copper and spores were on the same side of the membrane, the color that developed at 2.0 γ was darker where copper was in ionic form. Separation of adsorbed copper from the fungus by cellophane retarded this color development even more. At a concentration as high as 20 γ , maximum color was not attained in the usual 5-day incubation period under these conditions. Interestingly enough, with

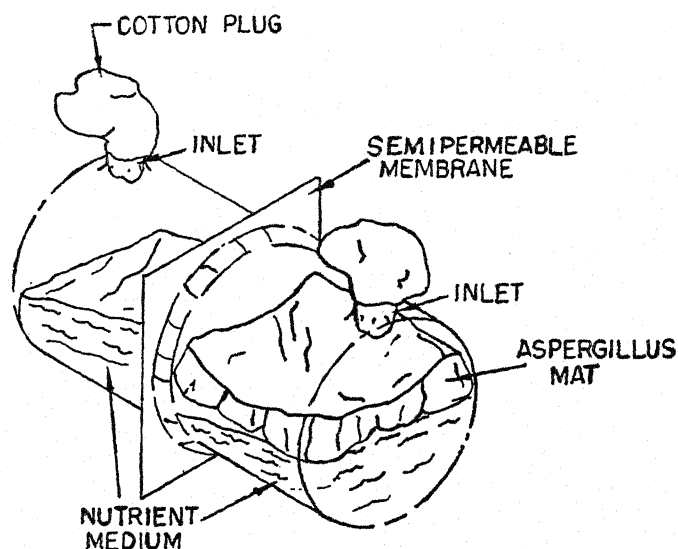


FIG. 5. PAIRED GLASS CELLS SEPARATED BY SEMIPERMEABLE MEMBRANE

further incubation, darker colors resulted from both the ionic and adsorbed copper systems, indicating that the membrane slows but does not stop passage of copper to the *Aspergillus* culture.

There is some preliminary evidence to show that combined agitation and heat fixes the element more securely to the surface of the resin. This treatment was observed to inhibit the rate of diffusion of the element even more than simple contact between resin and solution.

The depth of the medium in the cells is a further variable which may affect the availability of the copper for *A. niger*. In one experiment, most of the medium leaked out of a cell containing the fungus and 2 γ of adsorbed copper. From the resulting contact between spores and Amberlite, maximum spore color developed in 5 days. It would appear, therefore, that availability of a given concentration of copper for the fungus is retarded not only by adsorption and presence of a semipermeable membrane but also by depth of the medium.

The effects of valence and solubility on copper uptake by *A. niger* were studied with the following compounds: metallic copper flake, cuprous oxide, cupric oxide, and copper sulfate. These reagents were diluted with Aspergillus-leached Amberlite so that 0.01-gm. samples contained 0.1 γ copper. Leached-Amberlite was selected as a diluent because of its powdered form and absence of available copper. After bioleaching, the exchange capacity for copper is negligible and the resin makes an ideal diluent. Table 4 shows the amount of copper present in the 0.01-gm. samples as estimated by the *A. niger* method. Sampling error was high because of the several dilutions and weighings and, therefore, allowed only semi-quantitative evaluation. There is an indication, however, that all or most of the copper present, irrespective of valence or solubility, was taken up by the spores.

TABLE 4
Effect of valence and solubility of copper on uptake by A. niger

COPPER SOURCE CONTAINING 0.1 OF COPPER	COPPER ASSAYED	COPPER SOURCE CONTAINING 0.1 OF COPPER	COPPER ASSAYED
γ	γ	γ	γ
Cu ₂ O	0.6	CuSO ₄	0.8
	0.7		0.8
	0.7		0.8
Cu Flake	0.5	CuO	0.5
	0.6		0.5
	0.6		0.5

DISCUSSION

These studies on the *A. niger* method have not progressed far enough to allow validation of the assay as an index of crop response. The ability of the fungus, however, to develop color not only from ionic copper but in the presence of copper adsorbed on an ion-exchange resin, may indicate that the bioassay does simulate some of the conditions under which the element is taken up by plant roots. If further studies confirm the findings of previous investigators, the method is probably more reliable than chemical or spectrographic analyses of available copper. The sensitivity of the test is apparently accurate and, according to Acock, soil "sound" in respect to copper can be readily differentiated from "unsound" soils.

The bioassay is subject to certain disadvantages. Care must be taken to maintain the sensitivity of the stock strain of the organism. The small amounts of soil used in the assay necessitate keeping sampling errors at a minimum. Acid production by *A. niger* during the first 2 days of incubation may release more copper than is available to plants. Possibly this acidity allows uptake of adsorbed copper by the organism. The slow development of maximum color in the presence of adsorbed copper may be a function of the time required for the production of H ions, exchange of these ions with surface adsorbed copper, and subsequent diffusion of the released ions through the substrate to the Aspergillus culture.

RECOMMENDED PROCEDURES

Removal of sources of copper contamination in the laboratory

Errors in the assay introduced by copper contamination from the environment may be reduced to a minimum by observing the following precautions: (a) keep the laboratory free from dust, (b) store all copper reagents in a special cabinet, (c) handle large amounts of copper in other rooms, and (d) periodically clean the still used for preparing double-distilled water.

Preparation of glassware

All apparatus is made chemically clean by thorough washing with soap and water and immersion in cleaning solution. Rinsings with tap water are followed by immersion in 5 per cent acetic acid (prepared with double-distilled water). Glassware is finally rinsed with double-distilled water prepared from a Pyrex glass still. Petri dishes and pipettes are sterilized in the oven at 180°C. for 2 hours.

Preparation of medium

	I		II		III
Dextrose	50.0 gm.	NH ₄ HS	0.3 ml.	Fe citrate	0.055 gm.
KNO ₃	5.0 gm.	Norit	5 gm.	ZnSO ₄ ·7H ₂ O	0.02 gm.
		char-			
		coal			
MgSO ₄ ·7H ₂ O	1.0 gm.			MnSO ₄ ·4H ₂ O	trace
K ₂ HPO ₄	2.5 gm.			Na ₂ MoO ₄ ·2H ₂ O	trace

Dissolve I in 900 ml. double-distilled water and add II. Shake 5 minutes, filter, and adjust pH to 6 with concentrated HCl. Dissolve III and 100 ml. double-distilled water and combine with I. Autoclave 5 minutes at 105°C. Store in refrigerator.

Copper standards

The copper solution for preparing standard cultures of known copper content is prepared in three strengths: 10, 1.0, and 0.1 ppm. Copper foil or any copper compound that can be initially dissolved in HNO₃ may be used for this purpose. A 1-ml. graduated pipette is used for adding measured quantities of the standard to the culture dishes. The most practical range of copper standards for the assay is 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0 γ .

Inoculation

Stock cultures of *A. niger* are maintained in a vegetative state in soil previously tubed and sterilized. Subcultures are obtained by transfer of a loop of this soil to petri dishes containing the liquid medium and incubation for 5 days at 30°C. The spores from the resulting growth are washed off by adding more medium and agitating. This suspension is added to a liter of medium for dispensing. Routine analyses can be expedited by adding the medium to the plates with a sterile

15-ml. automatic pipette. Old standard cultures with light tan growth are a good source of copper-deficient spores. The spores retain their viability for a long time when stored in the refrigerator.

The usual bacteriological precautions are observed in all subculturing, pouring of plates, and inoculating.

Preparation of cultures for soil assay

The weight of the soil sample selected must necessarily depend upon the amount of copper estimated to be present. In most instances, however, 0.1–0.2 gm. weights are best. In a well-sampled soil, duplicate plates containing such weights usually agree well.

The finely divided dry soil is transferred to a sterile 9- by 2-cm. petri dish. To eliminate any molds that may be present, the soil is moistened with 0.5 ml. of 70 per cent alcohol (prepared with double-distilled water), covered for 1 hour, then the lid displaced and the dish warmed to 60°C. to evaporate the alcohol. Special care must be taken to spread the soil evenly over the bottom of the dish to avoid patchy cultures. Plates are then ready for addition of the preinoculated media. If soils or other copper sources to be assayed are difficult to wet, 1 drop of 1 per cent Tween 20 added to the culture will aid in distribution.

SUMMARY

The spore color sensitivity of *Aspergillus niger* to trace amounts of copper in soils was confirmed. The strain used had an accuracy of ± 0.01 in the 0 to 0.1 γ range, ± 0.025 in the 0.1 to 0.5 γ range and ± 0.05 in the 0.5 to 1.0 γ range.

Methods of minimizing copper contamination in the assay, selecting and maintaining copper-sensitive strains of the organism, and optimal physical conditions for growth are described.

The amount of copper in the substrate could be estimated either by interpretation of the spore color or by dry mycelial weights. Visual interpretation of spore color was most accurate with minimal depths of media; mycelial weights best reflected the copper concentration when larger volumes of media were used. The effects of surface area and depth of culture on sensitivity to copper were considered.

There is no apparent relationship between the bioassay for copper and chemical and spectrographic analyses.

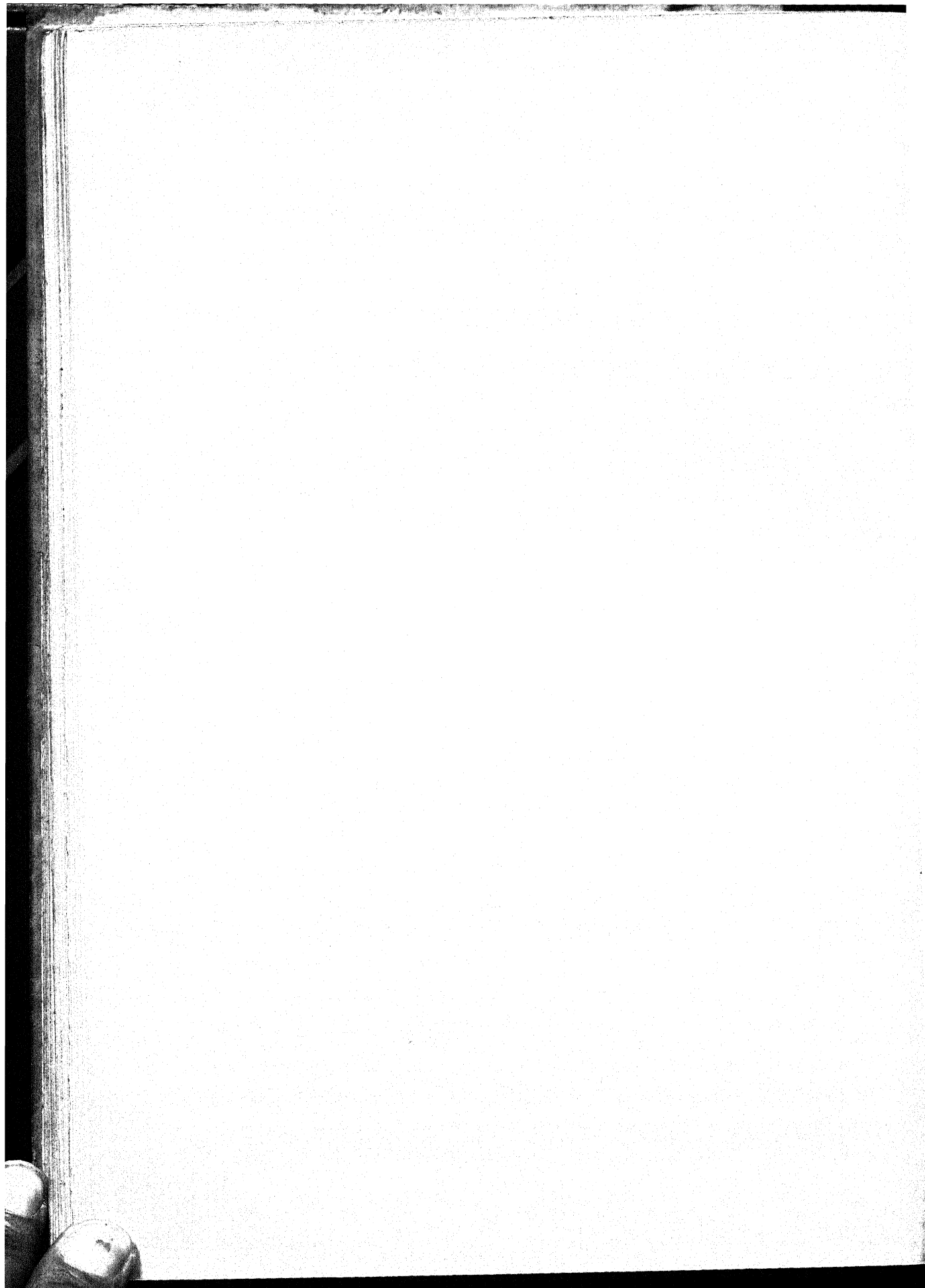
Preliminary studies on the mechanism of copper uptake by the fungus spores were made. The acid production by *A. niger* during the first 2 days of incubation was considered. Ionic copper was found to be readily available to the mold, as was adsorbed copper, although development of spore color is retarded with the latter.

A recommended procedure for routine assays for soil copper is described.

REFERENCES

- (1) Acock, A. M. 1941 An examination of Mulder's rapid biological method for estimating the amount of available copper in soils. *Aust. Council Sci. and Indus. Res. Jour.* 14: 288-300.

- (2) FOSTER, J. W. 1949 Chemical Activities of Fungi. Academic Press, New York.
- (3) MULDER, E. G. 1940 On the use of microorganisms in measuring a deficiency of copper, magnesium and molybdenum in soils. *Antonie van Leeuwenhoek* 6: 99-109.
- (4) MULDER, E. G. 1948 Microbiological estimation of copper, magnesium and molybdenum in soil and plant material. *An. Chim. Acta* 2: 793-800.
- (5) NICOLAS, D. J. D. 1949 Use of *Aspergillus niger* for the determination of mineral nutrients available in soils to crop plants. *Chem. and Indus.* (47): 809-810.
- (6) NICOLAS, D. J. D. 1950 Determining mineral nutrients. Microbiological aspects of bioassay. *Chem. Age* 62: 87-88.
- (7) NICOLAS, D. J. D. 1950 Use of *Aspergillus niger* for determining magnesium, copper, zinc and molybdenum in soils. *Jour. Sci. Food and Agr.* 1: 399-344.
- (8) NICOLAS, D. J. D., AND FIELDING, A. H. 1951 Use of *Aspergillus niger* (M) for the determination of magnesium, zinc, copper and molybdenum available in soils to crop plants. *Jour. Hort. Sci.* 24: 125-147.
- (9) STEINBERG, R. A. 1934 So-called "chemical stimulation" of *Aspergillus niger* by iron, zinc and other heavy metals. *Bul. Torrey Bot. Club* 61: 241-248.
- (10) STEINBERG, R. A. 1935 Nutritional requirements of the fungus, *Aspergillus niger*. *Bul. Torrey Bot. Club* 62: 81-90.
- (11) STEINBERG, R. A. 1935 Nutrient-solution purification for removal of heavy metals in deficiency investigations with *Aspergillus niger*. *Jour. Agr. Res.* 51: 413-424.
- (12) STEINBERG, R. A. 1945 Use of microorganisms to determine essentiality of minor elements. *Soil Sci.* 60: 185-189.



EFFECT OF FUMIGATION ON SOME CHEMICAL PROPERTIES OF SOILS¹

D. G. ALDRICH AND J. P. MARTIN

University of California Citrus Experiment Station

Received for publication July 27, 1951.

Since the work of Frank (2) in 1888, many investigators have suggested that the stimulation of plant growth which results from partial sterilization of the soil, both by heating and fumigation, is due in part to chemical changes in the soil. Early investigators (4, 11, 14, 15, 16) proposed many explanations based primarily on the production of beneficial organic compounds or destruction of toxic organic compounds. More recent investigators (3, 8, 13, 17) have tended to emphasize the change in inorganic constituents in the soil.

As previous reports from this laboratory (9, 10) have shown that soil fumigation markedly stimulated growth of citrus seedlings planted in old citrus soil, the present study was undertaken to determine some of the chemical changes that are produced in soil by fumigation and to evaluate these changes in relation to stimulated plant growth. Data obtained from a laboratory study of the effect of five volatile fumigants, and for comparative purposes, of steam sterilization, on some chemical properties of four soils are presented. The results of a few field studies are included.

MATERIALS AND METHODS

Four soils with the following physical and chemical properties were studied:

SOIL NO.	SOIL TYPE	MOISTURE* CAPACITY	<50 μ PARTICLES	pH SOIL PASTE	EXCHANGE CAPACITY	ORGANIC CARBON
		<i>per cent</i>	<i>per cent</i>		<i>me/100 gm.</i>	<i>per cent</i>
1	Yolo loam	50	46.6	7.7	18.0	0.93
2	Ramona sandy loam	31	36.8	6.5	8.0	0.35
3	Mountain soil	70	41.0	5.4	31.5	3.65
4	Hanford sandy loam	46	29.1	7.4	13.3	0.59

* Moisture capacity determined by Hilgard cup method (7).

The various fumigants after cooling in ice water were injected with a hypodermic syringe into 5-pound portions of sieved (2-mm. screen) soil in screw-cap bottles. Sufficient distilled water to bring the soil to 50 per cent of the moisture-holding capacity was immediately added to the soil in the bottles and the lids were tightly secured. After 3 days the soils were removed from the bottles and spread in a thin layer to air-dry.

The fumigants used and the amounts added to 5 pounds of air-dry soil were as follows:

¹ Paper No. 703, University of California Citrus Experiment Station. The authors wish to acknowledge the analytical assistance of Fred L. Whiting and Jarel O. Ervin during this investigation.

FUMIGANT	LOW DOSAGE		HIGH DOSAGE	
	ml./5 lb.	lb./acre-6 inch	ml./5 lb.	lb./acre-6 inch
D-D*.....	0.4	400	4.0	4000
Chloropicrin.....	0.2	200	2.0	2000
Carbon disulfide.....	0.6	600	6.0	6000
Propylene oxide.....	0.2	200	2.0	2000
Ethylene dibromide.....	0.14	200	1.4	2000

* Dichloropropane and dichloropropylene mixture.

The low dosage corresponds roughly to the amount of fumigant applied per acre commercially as a nematocide, larvicide, or fungicide. The high dosage rate corresponds to the amount which has given the best stimulation of growth of citrus replants in old citrus soil. For the steam-sterilization treatment, 5-pound portions of screened soil were autoclaved at 15 pounds pressure for 2 hours.

After air-drying, samples of soil from the various treatments were removed for chemical analysis. These samples are hereafter referred to as the 0-day incubation period. The remaining soil from each treatment was placed in wide-mouth 16-ounce jars in 420-gm. portions, adjusted to 50 per cent moisture capacity with distilled water, weighed, and incubated at room temperature. The lids were set loosely on the tops of the bottles. Subsequently, duplicate jars from the various treatments were removed for chemical analysis after 10, 20, 50, 100, and 250 days of incubation. The moisture content of the soils incubated for the longer periods was maintained at 50 per cent of capacity by periodic additions of distilled water sufficient to compensate for the loss by evaporation.

Ammonia nitrogen and numbers of bacteria, actinomycetes, and fungi were determined at the conclusion of the various incubation periods immediately upon removal of the moist soil from the jars. Determinations of nitrate nitrogen, water-soluble and exchangeable manganese, conductivity, pH, and analyses of saturation extracts of the variously treated soils for Ca, Mg, Na, K, PO_4 , SO_4 , Cl, CO_3 , and HCO_3 were made on soil samples that were allowed to air-dry following incubation. Ammonia and nitrate nitrogen were determined according to the methods of Harper (5, 6), analyses of saturation extracts according to Reitemeier (12), and manganese according to Willard and Greathouse (21). Conductivity and pH were determined, respectively, with an Aminco semimicroconductivity cell and a Beckman glass electrode assembly.

LABORATORY RESULTS

Since the most marked stimulation of citrus trees planted in old citrus soils is observed when fumigants are applied at high dosage rates, chemical data obtained at the low dosage rates are not reported. Fumigants applied at the low dosage rates, however, produced qualitative chemical changes similar to those obtained at the high rate of application, but these changes were consistently of smaller magnitude.

All treatments produced the typical partial sterilization effect on the soil

microbes, namely, destruction or near destruction of the soil organisms followed by a large increase in numbers upon incubation. In the alkaline soils numbers of fungi remained relatively low throughout the experiment. In the acid soils they reestablished themselves in relatively large numbers.

The effects of the various fumigants and of steam sterilization on the ammonia and nitrate composition of four soils after various periods of incubation are shown in figure 1. With the exception of soil 3, which is strongly acid, no ammonia nitrogen was found in the untreated (check) samples of the soils after the 0-day incubation period. At the end of 50 days' incubation, nitrification of ammonia in the untreated sample of soil 3 was essentially complete. Fumigation, on the other hand, produced the well-known and often reported (20) partial steriliza-

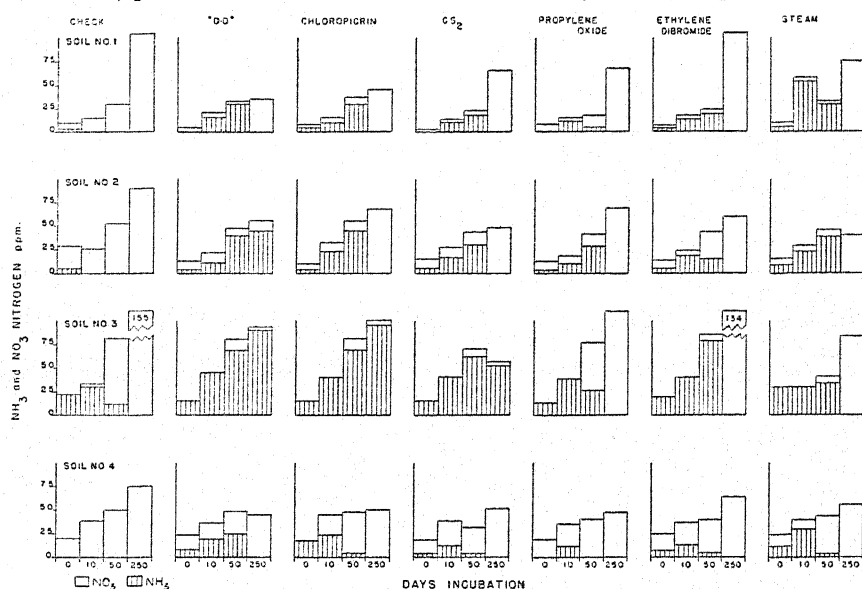


FIG. 1. EFFECT OF FUMIGATION AND STEAM STERILIZATION ON NH_3 AND NO_3 CONTENT OF FOUR INCUBATED SOILS

tion or sterilization effect on the inorganic nitrogen of the soil, namely, an increase of ammonia followed by nitrification of the ammonia to nitrate. Nitrification of ammonia produced by fumigation occurred most rapidly in soil 4, an alkaline sandy loam, and most slowly in soil 3, an acid mountain soil of high organic matter content. A comparison of the relative effects of the various fumigants on the ammonia and nitrate content of the soils reveals that complete nitrification of ammonia was accomplished in a shorter period of incubation when the soil was fumigated with propylene oxide and ethylene dibromide. Generally, nitrification proceeded most slowly where "D-D" was applied. Although fumigation produced a marked change in the proportion of ammonia to nitrate nitrogen when fumigated soils were compared with untreated soils, the sum of these two forms of inorganic nitrogen was never greater than the nitrate content of the untreated soils at the end of the 250-day incubation period.

Chemical analysis of the saturation extracts of the untreated and fumigated soils shed further light on the effect of partial sterilization on the chemical composition of the soil. Figure 2 shows that without exception partial sterilization increased the quantity of soluble Ca, Mg, and K in each soil studied, and that the amount of increase was greatest for Ca followed in order generally by Mg and K. Data for Na are not reported because the amount present in these soils was so small that negligible quantities were found in the saturation extracts. In the check treatment the amounts of Ca, Mg, and K in the extracts increased with time and appeared coincident with the rate of nitrate formation. A similar relationship between solubility and incubation time was suggested in the sterilized soils, but close examination of figure 2 shows that the greatest difference in chem-

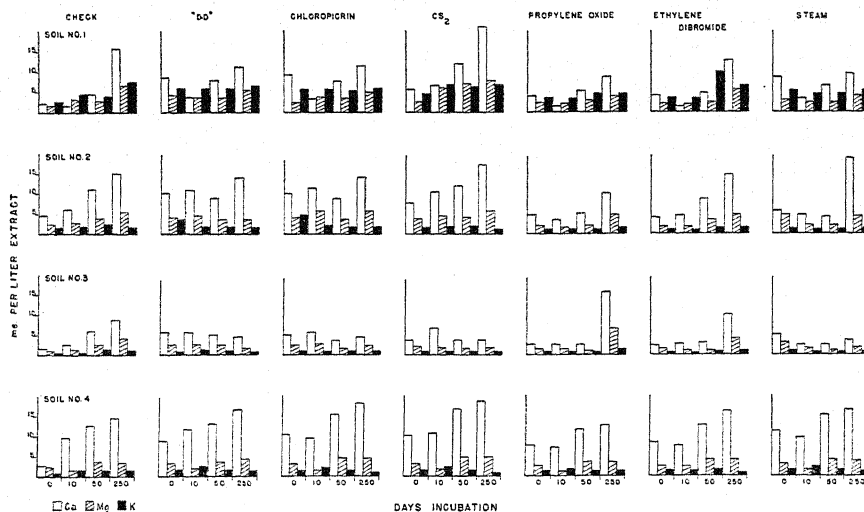


FIG. 2. EFFECT OF FUMIGATION AND STEAM STERILIZATION ON THE CA, MG, AND K CONTENT OF THE SATURATION EXTRACTS OF FOUR INCUBATED SOILS

ical composition between sterilized and untreated soils usually occurred at the 0-day incubation period. The relatively smaller amounts of cations found in the extracts of soil 3 can be accounted for readily by the acid nature of the soil. When the amounts of Ca, Mg, and K solubilized by the various partial sterilization treatments were used as a basis of comparison, it appeared that propylene oxide and ethylene dibromide produced the least chemical change, while CS_2 produced the greatest change. Steam sterilization, chloropicrin, and "D-D" treatments produced changes somewhat between the extremes.

Although pH, Cl, SO_4 , PO_4 , CO_3 , and HCO_3 were determined in every extract, these data with the exception of a few typical data for Cl and SO_4 are omitted because no difference attributable to treatment could be found. The effects of fumigants containing chlorine on the chloride content of the extracts of a fumigated and an untreated soil (soil 1) are shown in figure 3. As would be expected, the chloride content of the extract from the untreated soil remained low and

essentially constant throughout the incubation period, whereas treatment of the soil with chlorinated hydrocarbons raised the chloride content of the extract starting with 0-day incubation. After the 0-day incubation period the chloride content of the extract of soil treated with chloropicrin rose to a maximum at 10 days' incubation and remained relatively constant thereafter for 250 days. Fumigation with "D-D," on the other hand, resulted in a chloride content at 0-day incubation that was less than that produced by chloropicrin. Unlike chloropicrin, the chloride content of the extract fell slightly at 10 days but then rose sharply and continuously for 250 days.

With the exception of CS_2 , none of the partial sterilization treatments used in this investigation produced significant changes in the sulfate composition of

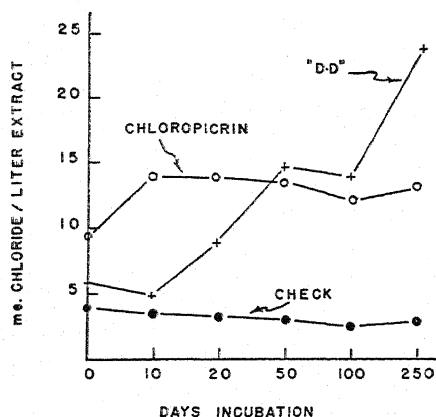


FIG. 3

FIG. 3. EFFECT OF FUMIGATION WITH CHLOROPICRIN AND "D-D" ON CHLORIDE CONTENT OF SOIL 1

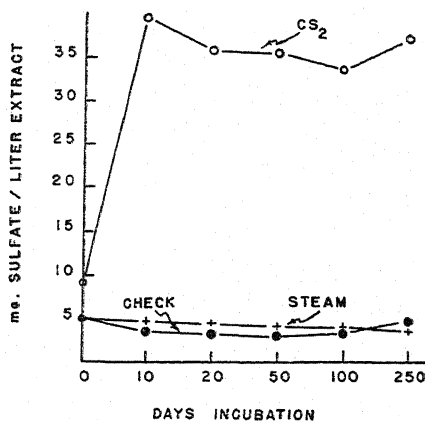


FIG. 4

FIG. 4. EFFECT OF FUMIGATION WITH CS_2 ON SULFATE CONTENT OF SOIL 1

the extracts. A typical set of data obtained from an untreated, a steam-sterilized, and a CS_2 -fumigated soil (soil 1) is shown in figure 4. No particular change in the sulfate composition of the extract from the check or steam-sterilized soil occurred during the 250-day incubation period, whereas a substantial increase in sulfate, especially after 10 days' incubation, occurred in the CS_2 -treated soil.

The data presented in table 1 show the effect of fumigation and steam sterilization on the water-soluble plus exchangeable manganese content of the soils. Differences in the amounts of these two forms of manganese between treated and untreated samples of the four soils were greatest at 0-day incubation. As the period of incubation increased to 250 days the soluble plus exchangeable manganese decreased appreciably in all soils regardless of treatment. In soils 1 and 4, which are alkaline, no water-soluble or exchangeable manganese was found at the end of 250 days' incubation. Some of these two forms of manganese were found in acid soils 2 and 3 throughout the incubation period, the amounts being particularly high during the first 50 days of incubation in soil 3, which is

TABLE 1
Influence of fumigation on water-soluble* plus exchangeable† manganese content of soils
In ppm. soil

TREATMENT	MANGANESE CONTENT OF SOIL					
	0 days	10 days	20 days	50 days	100 days	250 days
<i>Soil 1</i>						
Check.....	3.0	6.5	5.0	0	1.7	0
"D-D".....	6.5	12.5	9.1	1.2	2.0	0
Chloropicrin.....	7.0	12.2	10.3	9.8	3.0	0
CS ₂	27.0	23.0	22.0	16.5	5.8	0
Propylene oxide.....	4.6	9.0	7.0	3.0	2.7	0
Ethylene dibromide.....	3.2	8.7	6.3	2.8	1.3	0
Steam.....	17.0	14.0	13.0	9.0	7.8	0
<i>Soil 2</i>						
Check.....	4.3	2.4	2.2	2.7	2.4	4.6
"D-D".....	39.5	44.6	44.6	23.7	7.7	5.8
Chloropicrin.....	47.1	48.8	45.8	6.1	5.4	8.9
CS ₂	59.6	62.3	56.9	5.0	4.3	6.3
Propylene oxide.....	22.0	15.5	5.6	3.8	6.1	4.9
Ethylene dibromide.....	23.3	6.5	2.8	5.9	3.7	3.7
Steam.....	57.2	53.2	53.8	33.8	9.3	13.4
<i>Soil 3</i>						
Check.....	31.5	6.6	8.8	0	6.3	6.9
"D-D".....	53.2	95.6	109.0	88.3	7.4	4.9
Chloropicrin.....	60.5	98.6	114.4	141.0	56.9	14.8
CS ₂	150.0	156.0	131.1	19.2	7.4	5.7
Propylene oxide.....	41.5	10.5	8.2	3.8	5.8	6.5
Ethylene dibromide.....	48.8	18.2	11.4	0	4.3	6.8
Steam.....	209.0	170.0	108.0	207.0	115.0	110.3
<i>Soil 4</i>						
Check.....	0.8	0	1.9	0	0	0
"D-D".....	5.9	7.9	8.8	4.2	5.5	0
Chloropicrin.....	6.8	7.2	8.5	3.1	3.8	0
CS ₂	20.2	15.5	14.4	1.4	2.5	0
Propylene oxide.....	2.8	4.1	3.2	0	0	0
Ethylene dibromide.....	2.7	0	3.1	0	0	0
Steam.....	14.1	8.3	9.6	1.5	2.5	0

* Water-soluble manganese determined on a 1:2.5 soil-water extract.

† Exchangeable manganese determined, on sample free of water-soluble manganese, by leaching with neutral *N* ammonium acetate.

strongly acid (pH 5.4). So far as the effect of a particular sterilizing treatment is concerned, steam sterilization and CS₂ fumigation released the greatest amount of manganese, whereas propylene oxide and ethylene dibromide released little

more manganese than that present in the untreated soils. Chloropicrin and "D-D" released somewhat intermediate amounts.

FIELD RESULTS

During the course of the investigations conducted by this laboratory on the effect of soil fumigation on growth of citrus trees planted in old citrus soils, chemical data were obtained from field plots treated with various fumigants. The similarity between the chemical changes produced in the field and the laboratory data reported in the preceding sections of this paper is worthy of note, especially since the chemical changes produced by fumigation in the field appeared to last for many months. Analyses of saturation extracts of soil from the 0-1-foot

TABLE 2
Chemical analysis of saturation extracts of soils from three fumigated field plots

CONSTITUENT	PLOT 1U*		PLOT 1C†		PLOT 4C†	
	Fumigated	Not Fumigated	Fumigated	Not Fumigated	Fumigated	Not Fumigated
Ca.....me./l.	8.4	3.5	9.8	4.3	9.1	7.8
Mg.....me./l.	7.5	4.3	7.3	4.6	8.1	7.2
Na.....me./l.	0.6	4.0	6.8	5.6	7.5	6.7
K.....me./l.	1.1	0.8	0.7	0.5	0.3	0.4
SO ₄me./l.	13.4	8.0	17.1	13.0	23.0	20.3
Cl.....me./l.	3.4	1.4	6.3	3.0	4.5	4.1
CO ₃me./l.	0	0	0	0	0	0
HCO ₃me./l.	2.1	3.0	2.0	1.9	1.6	1.7
P.....ppm.	3.0	6.0	9.8	9.8	3.3	4.0
K × 10 ³	2.8	1.9	3.6	2.2	3.3	3.0
pH.....	7.1	7.1	7.1	7.2	6.9	6.9

* Plot 1U sampled 1 year after fumigation with CS₂.

† Plots 1C and 4C sampled 2½ years after fumigation with "D-D."

depths of three field plots fumigated with CS₂ or "D-D" and sampled 1 or 2½ years after treatment are reported in table 2. Each plot is on a different soil and was planted to lemons at the time of sampling. Fumigation increased the Ca, Mg, SO₄, and Cl content of the extracts of soils from each plot. In two of the three plots K and Na were increased by fumigation and P was decreased. The increased solubility of ions resulting from fumigation was manifested by a higher conductivity in the extract from the fumigated plots than in those from the untreated plots.

DISCUSSION

This study has revealed that the nature and magnitude of the chemical changes produced by sterilization treatments are dependent upon the soil and the kind of sterilizing agent. Thus, nitrification of ammonia produced by ammonification following partial sterilization began sooner in a sandy alkaline soil than in an

acid mountain soil high in organic matter. Generally, nitrification began earlier when propylene oxide or ethylene dibromide was used to fumigate the soil than when "D-D," chloropicrin, CS_2 , or steam was used. Apparently the latter treatments were more effective in destroying the nitrifying bacteria of the soil than was propylene oxide or ethylene dibromide. Possibly, also, the difference in the effects of the various fumigants on nitrification can be attributed partly to differences in the physical and chemical properties of the fumigants. Propylene oxide and ethylene dibromide produce a minimum chemical change in the soil. Thus the physicochemical properties of the treated soil are not altered materially from those of the untreated soil. Nitrifying bacteria not killed by the treatment, or through recontamination, could establish an active population in a relatively short time. On the other hand, "D-D," chloropicrin, and CS_2 , like steam sterilization, produce pronounced chemical changes in the soil which may retard the reestablishment of the nitrifying bacteria.

Though some investigators (18, 19) have reported that steam sterilization or fumigation produces an increase in the amount of nitrogen present as ammonia or nitrate or both, this study has revealed that, with the soils used, partial sterilization altered only the proportion of ammonia to nitrate nitrogen and not the total amount of the two forms.

The quantity of soluble calcium and, to a lesser degree, magnesium and potassium found in saturation extracts of treated soils was increased substantially at 0-day incubation by fumigation with CS_2 , "D-D," and chloropicrin and by steam sterilization. The difference between the Ca, Mg, and K content of extracts from treated and untreated soils became relatively small as the incubation time increased, although the amounts of these cations extracted from the untreated soils became substantially greater at the end of 250 days' incubation. Fumigation with propylene oxide and ethylene dibromide produced only minor increases in the quantity of Ca, Mg, and K extracted at 0-day incubation, and at subsequent incubation periods little if any difference between the cation content of extracts from treated and untreated soils was noted. As microbial assays of the treated soils showed all partial sterilization treatments had virtually eliminated microbial activity at the 0-day incubation period, the pronounced chemical changes produced by certain treatments at that time must be attributed to a direct chemical reaction of the partial sterilizing agent with the soil and not to microbial activity. When the effect of increasing length of incubation period on the quantity of cations extracted is considered, a comparison of the data for ammonia and nitrate production with the data for extracted Ca, Mg, and K suggests that the solubility of soil compounds containing these ions is in some manner influenced by microbial activity coincident with the nitrification process. As the quantity of nitrates in a particular soil and treatment increases, a fairly consistent increase in the amounts of Ca, Mg, and K found in the saturation extracts also is observed. This relationship may be ascribed in part to the effect of acidification on the solubility of various basic soil constituents, since it has been shown (1) that a decrease in pH value occurs in the soil prior to nitrate formation.

The influence of partial sterilization by fumigation and steam treatment on the water-soluble and exchangeable manganese content of the soil appears to be primarily the result of a direct chemical reaction between the sterilizing agent and the soil, since the greatest quantity of these forms of manganese are found at the 0-day incubation period. As the length of the incubation period increases, the amount of water-soluble plus exchangeable manganese continually decreases. A calculation of the amount of manganese that could possibly be released by the decomposition of the organic matter present in the soil reveals that the soil organic matter is not the main source of the soluble plus exchangeable manganese. This would indicate that most of the manganese made available by partial sterilization of these soils is derived from inorganic sources. In line with previously noted effects, treatment with propylene oxide and ethylene dibromide produced the least amount of manganese, whereas CS_2 and steam produced the greatest amount.

With the exception of fumigants that contain either chlorine or sulfur, this laboratory study shows that fumigation produced little effect on the anion composition of the extracts from sterilized soils. As CS_2 is decomposed in the soil, sulfates are formed. In like manner, as chlorinated hydrocarbons are decomposed, chlorides are liberated. A comparison of the chloride data obtained from chloropicrin and "D-D" suggests that "D-D" is more stable or more strongly adsorbed by the soil, or both, than is chloropicrin, since in the "D-D"-treated soil, chlorides are released slowly up to 10 days' incubation but increase sharply and continuously in amount thereafter throughout the entire incubation period. Chloropicrin, on the contrary, produces its maximum chloride content within 10 days' incubation, the amount remaining constant for the ensuing incubation time. Since chlorides are particularly toxic to plants, some attention should be paid to the amount of chlorinated hydrocarbons used for soil sterilization. Experience at this laboratory has shown that on occasions sufficient quantities of chlorides have been released in the soil upon decomposition of the fumigant to injure plants severely. A leaching treatment to remove the chlorides from the soil eliminated the cause of the injury and allowed proper subsequent growth.

Analyses of saturation extracts of soils from field plots fumigated with CS_2 or chloropicrin taken 1 or 2½ years after treatment show that the chemical changes produced in the field by fumigation are similar to those produced in the laboratory. It is difficult to understand, however, why these chemical differences persist in the field so long after treatment, for adsorption of nutrients by plants and leaching of nutrients by irrigation and rain water would certainly tend to obliterate the changes resulting from the fumigation treatment. An attempt to clarify this relationship is now in progress.

In light of the foregoing information and of data which are to be published on the influences, on the nutrient composition of citrus plants, of chemical changes resulting in the soil from fumigation, it appears that stimulated growth of citrus planted in old citrus soil cannot be attributed to an increased nutrient supply. Though the quantity of nutrient ions solubilized has been increased immediately upon fumigation, the increase has not raised the supply of

nutrients from a deficient level to a sufficient level. All nutrients reported in this paper appeared, on the basis of current information concerning the nutrient requirements of citrus, to be adequate in supply prior to treatment. In view of the chemical changes produced by partial sterilization, there is a distinct possibility, however, that in some soils the nutrient supply may be raised from a deficient level to a sufficient level, thereby producing increased plant growth. In other soils the nutrient supply may be raised from an adequate level to a toxic level, resulting in decreased plant growth. These two possibilities have been suggested and corroborated by the work of Fujimoto and Sherman (3) on the effect of steam sterilization on the solubility of manganese.

SUMMARY

A study has been made of the chemical changes produced by partial sterilization of four soils with five volatile fumigants and, for comparative purposes, with steam. Treatment with steam, chloropicrin, "D-D," CS_2 , propylene oxide, and ethylene dibromide produced an initial increase in the ammonia nitrogen in the soil, which on incubation was oxidized to nitrates. The onset of nitrification appeared to be influenced by the nature of the soil and the sterilizing agent.

Fumigation with "D-D," chloropicrin, and CS_2 and steam sterilization produced substantial changes in the amounts of Ca, Mg, K, and Mn in extracts of the treated soils. Propylene oxide and ethylene dibromide produced only a small change in the solubility of these cations.

The anion composition of extracts of treated soils appeared to be affected only when the fumigant contained a compound such as chlorine or sulfur which was released upon decomposition of the fumigant in the soil.

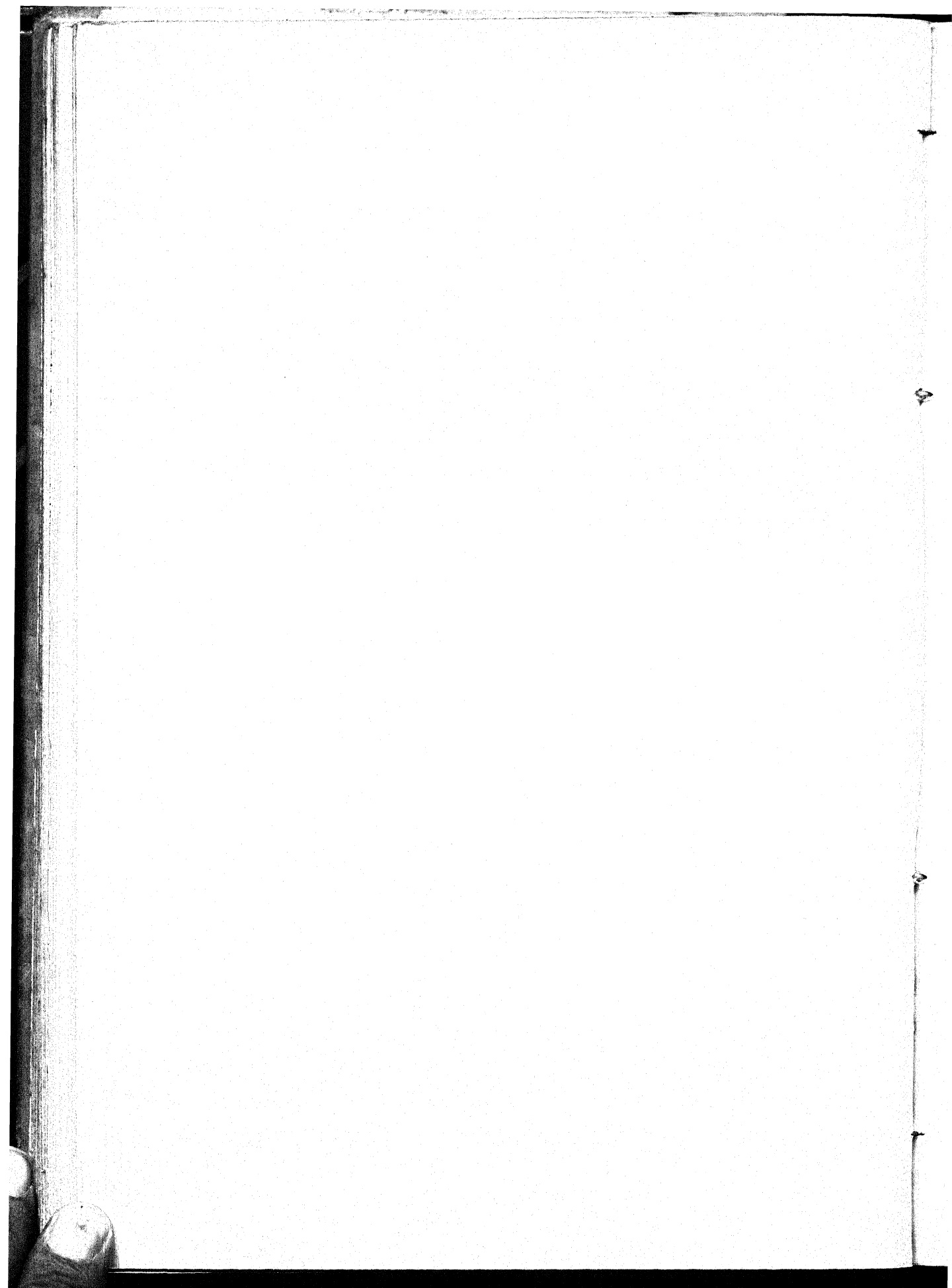
When the influence of incubation time following fumigation is considered in relation to the magnitude of the chemical change produced by sterilization, it appears that the most pronounced chemical differences between treated and untreated soils were the result of direct chemical reactions between the sterilizing agent and the soil. Quantitative chemical changes that occurred with increasing incubation time appear related to the nitrification process.

It is concluded from the evidence presented that the stimulation of citrus plants grown in fumigated old citrus soils cannot be attributed to increased nutrient availability, although that possibility definitely exists where other crops and certain soil types are involved.

REFERENCES

- (1) CASTER, A. B., MARTIN, W. P., AND BUEHRER, T. F. 1942 Microbiological oxidation of ammonia in desert soils: I. Ariz. Agr. Exp. Sta. Tech. Bul. 96.
- (2) FRANK, A. B. 1888 Über den Einfluss welchen das Sterilisiren des Erdbodens auf die Pflanzen-entwicklung ausübt. *Ber. Deut. Bot. Gesell. (Generalversammlungs Heft)*. 6: 87-98.
- (3) FUJIMOTO, C. K., AND SHERMAN, G. D. 1948 Manganese availability as influenced by steam sterilization of soils. *Jour. Amer. Soc. Agron.* 40: 527-534.
- (4) GRIEG-SMITH, R. 1911 Bacteriotoxin and the agricere of soil. *Centbl. Bakt. (II)* 30: 552.
- (5) HARPER, H. J. 1924 Determination of ammonia in soils. *Soil Sci.* 18: 409-418.

- (6) HARPER, H. J. 1924 Accurate determination of nitrates in soils. *Jour. Indus. and Engin. Chem.* 16: 180-183.
- (7) HILGARD, E. W. 1906 Soils. The Macmillan Co., New York.
- (8) KELLEY, W. P., AND McGEORGE, W. T. 1913 Effect of heat on Hawaiian soils. *Hawaii Agr. Exp. Sta. Bul.* 30.
- (9) MARTIN, J. P. 1948 Effect of fumigation, fertilization, and various other soil treatments on growth of orange seedlings in old citrus soils. *Soil Sci.* 66: 273-288.
- (10) MARTIN, J. P. 1950 Effect of fumigation and other soil treatments in the greenhouse on the fungus population of old citrus soils. *Soil Sci.* 69: 107-122.
- (11) PICKERING, S. U. 1908 Action of heat and antiseptics. *Jour. Agr. Sci.* 3: 32-54.
- (12) REITEMEIER, R. F. 1943 Semimicroanalysis of saline soil solutions. *Indus. and Engin. Chem., Analyt.* Ed. 15: 393-402.
- (13) ROBINSON, R. R. 1944 Inhibitory plant growth factors in partially sterilized soils. *Jour. Amer. Soc. Agron.* 36: 726-739.
- (14) SCHREINER, O., AND REED, H. S. 1907 Some factors influencing soil fertility. U. S. Dept. Agr. Bur. Soils Bul. 40.
- (15) SCHREINER, O., AND REED, H. S. 1907 Certain organic constituents of soils in relation to soil fertility. U. S. Dept. Agr. Bur. Soils Bul. 47.
- (16) SCHREINER, O., AND LATHROP, E. C. 1912 On the growth of plants in partially sterilized soils. *Jour. Amer. Chem. Soc.* 34: 1242-1259.
- (17) SHERMAN, G. D., AND FUJIMOTO, C. K. 1947 Effect of the use of lime, soil fumigants, and mulch on the solubility of manganese in Hawaiian soils. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 206-210.
- (18) STARKEY, R. L., AND WAKSMAN, S. A. 1923 Partial sterilization of the soil, microbiological activities and soil fertility. II. *Soil Sci.* 16: 247-268.
- (19) STARKEY, R. L., AND WAKSMAN, S. A. 1923 Partial sterilization of the soil, microbiological activities and soil fertility. III. *Soil Sci.* 16: 343-357.
- (20) WAKSMAN, S. A., AND STARKEY, R. L. 1923 Partial sterilization of soil, microbiological activities and soil fertility. I. *Soil Sci.* 10: 137-157.
- (21) WILLARD, H. H., AND GREATHOUSE, L. H. 1917 Colorimetric determination of manganese by oxidation with periodate. *Jour. Amer. Chem. Soc.* 39: 2366-2377.



BOOKS

Advances in Agronomy. Volume 3. Edited by A. G. NORMAN. Academic Press Inc., New York, 1951. Pp. 361. Price \$7.80.

Prepared under the auspices of the American Society of Agronomy, this third volume of the series contains an excellent set of reviews by G. W. Burton, H. J. Harper, J. A. McMillan, R. Q. Parks, R. F. Reitemeier, R. W. Simonson, A. L. Taylor, C. J. Willard, and E. Winters. The subjects covered are subsoil, alfalfa meadows, soil potassium, agriculture in England, grasses for southeastern states, nematode control, soil conservation, and irrigation. Each of these men has brought his thinking from many years of study of the subject to bear in the preparation of his paper. The review of soil conservation by Harper is of special importance in that it gives a clear picture of the development of this movement in the United States by a man who, although he has no connection with the Soil Conservation Service, is thoroughly familiar with the problems and knows what has been and what should be done about them. But all of these reviews merit study. A new departure in this volume is the article by McMillan, of the Ministry of Agriculture and Fisheries of England, discussing the effects of war on the agriculture of England and Wales. The editor and advisory board are to be congratulated on the quality of the material in this volume.

Animal Nutrition. Third Edition. By LEONARD A. MAYNARD. McGraw-Hill Book Company, Inc., New York, 1951. Pp. 474, figs. 47. Price \$6.50.

The principles of nutrition and their application to the feeding of farm animals are presented in a concise manner in the revised edition of this well-known book. Some changes have been made in each chapter, but the major revisions are in the discussions on enzymes, isotopes, trace elements, vitamins, and growth relationships. The book is intended primarily as a classroom text. The subject is presented under four major divisions: general bases of nutrition, nutrients and their metabolism, measurement of body needs and feed values, and nutritive requirements for body processes and productive functions. A list of selected references is appended to each chapter, and supplemental references are given as footnotes. The appendix contains a visual-aid bibliography and an author and subject index. The book is highly useful for reference and is entitled to a wide reading.

Annual Review of Microbiology. Volume 5. Edited by CHARLES E. CLIFTON, SIDNEY RAFFEL, AND H. ALBERT BARKER. Annual Reviews, Inc., Stanford, California, 1951. Pp. 379. Price \$6 plus shipping charges (15 cents in U. S. A. and 35 cents elsewhere).

The 19 subjects covered in this volume include morphology, cytology, enzymatic adaptation, metabolism, and nutrition of bacteria and fungi, nutrition and metabolism of protozoa, physiology of algae, endotoxins, mode of action of antibiotics, plant chemotherapy, pathological plant growth, virus-induced tumors of animals, physical and chemical characteristics and interference phenomena of

viruses, poliomyelitis, and microbial deterioration of manufactured materials. All of these subjects are well reviewed by capable scientists in these several fields of research. The chapter on plant chemotherapy, by J. G. Horsfall and A. E. Dimond, is of special interest to soil-plant scientists. There is hope of disease and insect control by such procedures. A long bibliography is appended to each review, the number of authors listed in the index totaling some 2,300 for the entire volume. This is a highly valuable review. The type is a little too small for rapid reading.

British Scientists. By E. J. HOLMYARD. The Philosophical Library, Inc., New York, 1951. Pp. 88, portraits, 24. Price \$2.75.

The author of this attractive little volume has presented thumbnail sketches of Bacon, Gilbert, Napier, Harvey, Boyle, Newton, Hutton, Black, Priestley, Cavendish, Dalton, Davy, Herschel, Faraday, Darwin, Kelvin, Maxwell, Lester, Crookes, Perkin, Dewar, Ramsay, Thompson, and Rutherford, all men of whom the British may well be proud. The last three chapters deal with the structure of the atom, the approach to the present day, and British scientific societies. A select biographical bibliography is appended.

Elements of Plant Protection. By LOUIS PYENSON. John Wiley and Sons, Inc., New York, 1951. Pp. 538, figs. 226. Price \$4.96.

This photo-offset edition is one of the Wiley Farm Series, which is designed more for use in short courses in agriculture, for students in vocational agriculture, and for farmers than for students in the regular courses in colleges of agriculture. The first 10 chapters deal with the structure, development, life history, and control of insects, the next two with bird and animal pests, the next six with plant diseases and their control, the next seven with weeds and their eradication, and the last three with equipment and its care and use. A list of questions for discussion is appended to each chapter. The appendix contains a selected list of reference books and a very good glossary. The illustrations are well chosen. The book should serve a very useful purpose.

Experiments in Soil Bacteriology. Revised Edition. By O. N. ALLEN. Burgess Publishing Company, Minneapolis, 1951. Pp. 127. Price \$2.50.

This is an offset-printed manual with a cardboard cover and ring binder. It is essentially the same manual as that reviewed in SOIL SCIENCE 68: 412, 1949, with a few new references and the addition of practical soil tests for nitrates and potassium.

Grasses of Wisconsin. By NORMAN C. FASSETT. University of Wisconsin Press, Madison, 1951. Pp. 173, figs. 353. Price \$3.

The author has made a careful study of the native grasses of Wisconsin and those that have escaped from cultivation and propagate without man's help. The characteristics of each grass are given and its distribution is shown on a Wisconsin map. The large number of excellent and detailed drawings of the

grasses and their several parts make this a highly useful reference work. A glossary and an extended index are appended. Many days of very careful work have gone into the preparation of this important book.

An International Index of Films on the Conservation and Utilization of Resources.

By United Nations Film Board. Columbia University Press, New York, 1950.

Pp. 175. Price, paper-bound, \$1.

The list of films shown in this index was prepared under the direction of the United Nations Film Board by UNESCO and the United Nations Department of Public Information, Films, and Visual Information Division. The Index gives the subject of each film, a short description of its content, and the source from which it may be obtained. Although a large percentage of the films deal with American resources, a number of them have been developed in other countries. Most of them are in black and white, but a few are in color.

Manual of Bacterial Plant Pathogens. Second Edition. By CHARLOTTE ELLIOTT.

The Chronica Botanica Co., Waltham, Mass., and Stechert-Hafner Inc., New York, 1951. Pp. 186. Price \$6.

This is volume 10 of "Annales Cryptogamici et Phytopathologici." It is "dedicated to the members of Erwin F. Smith's laboratory who pioneered in the study of bacterial diseases in plants." It begins with a reproduction of the first page of Professor T. J. Burrill's report on his discovery that fire blight in pear was of bacterial origin, the first case on record. The remainder of the book lists all the known bacterial plant pathogens, their synonyms, cultural, morphological, and physiological characteristics, diseases they cause, means by which these diseases can be controlled, and literature related thereto. The book is divided into two parts, the first dealing with proved pathogens, and the second with those reported in the literature but not yet recognized as valid. A number of excellent illustrations are shown. The book represents a large amount of painstaking work and is invaluable for workers in this field of research.

Manual of Phycology. Edited by GILBERT M. SMITH. The Chronica Botanica

Company, Waltham, Mass., and Stechert-Hafner, Inc., New York, 1951. Pp. 375, figs. 48. Price \$7.50.

This introduction to the algae and their biology constitutes volume 17 of "A New Series of Plant Science Books." The 17 contributors include the best-known American and European specialists in their field of research. The 17 chapters have to do with the history of phycology, classification of algae, studies of the several divisions of algae, the cytology, sexuality, pigments, physiology, and ecology of the several forms, and plankton algae. The appendix contains methods for cultivation and microtechniques. Among the more interesting phases of the subject for the soil-plant scientist is the discussion about the ability of algae to fix nitrogen, with evidence that certain species can do this. The chapter on the biology of plankton contains some very important information on organic-matter production in relation to the needs of the zooplankton. An average value

of 3.2 tons dry weight of plankton an acre annually is arrived at, with some values as high as 10 tons an acre. The methods of cultivation of algae shown are also of great interest. This book fills a highly important need.

Microbial Decomposition of Cellulose. By RALPH G. H. SIN. Reinhold Publishing Corporation, New York, 1951. Pp. 531, figs. 128. Price \$10.

The primary concern of the author of this book is with cotton textiles and the losses that are sustained through microbial attack. But he deals with fundamentals as well as applications. The 12 chapters are grouped under introduction, structure and properties of cotton fabrics, causal organisms, mechanism of degradation, and methods of prevention. The discussion on the nature and properties of the cellulose molecule is of special interest, as is that part which has to do with the use of toxic inhibitors. Each chapter is followed by a long list of references, the work of more than 2,000 authors being reviewed in the book as a whole. This is undoubtedly the most complete presentation of the subject that has ever been published. Readers will find themselves very much indebted to the author for having compiled and arranged the material so effectively.

The Molds and Man. By CLYDE M. CHRISTENSEN. University of Minnesota Press, Minneapolis. Pp. 244. Price \$4.

This popularly written introduction to the fungi tells how these organisms grow, reproduce, form partnerships with other plants and with animals, effect parasitism, and provide useful products for industrial purposes. The last chapter shows a classification of the fungi. Among the more interesting features of the book are the discussions of the nature of "all-permeating, mouth-watering, tantalizing, with the promise of Elysian enjoyment, a condensation of all that is good and noble" truffles, and the method of harvesting them, ants that cultivate fungi for their own uses, such troublesome fungi as those responsible for ringworm and athlete's foot, and the more useful types that develop the special qualities of Roquefort cheeses and their American analogues. This is a very readable and interesting book.

On Consolidation and Settlement of Loaded Soil Layers. By K. V. HELENELUND. Geotechnical Department Finnish State Railways, Helsinki, 1951. Pp. 209, figs. 93.

This publication is in Finnish, but the legends for the figures, an extended summary, a synopsis, and explanations of symbols are presented in English. The points covered are stress distribution, compressibility, progress of consolidation, time-settlement curve, coefficient of consolidation, water-content curves, and some miscellaneous observations. A list of some 125 references is appended. Soil technologists will find this publication of considerable interest.

Plant Growth Substances. Edited by FOLKE SKOOG. University of Wisconsin Press, Madison, 1951. Pp. 476. Price \$6.

In celebration of the 100th anniversary of the founding of the University of

Wisconsin, a symposium on plant growth substances was presented by 40 workers in this field of research. This book contains the papers that were read. It also contains photographs of a considerable number of the speakers. For convenience, the papers are grouped under the headings: plant growth substances, growth substances in plant metabolism, tissue response, vegetative development, reproductive development, and pathological growth, practical applications of growth regulators, and vitamins and amino acids as growth factors. With one exception, Hans Burström, University of Lund, Sweden, the authors are all members of staffs of American universities and other research units. Rapid growth in the development of this subject is indicated by the fact that several thousand research specialists are now engaged in one or another aspect of the problem. Every worker in this and closely related fields will want a copy of this highly significant volume for ready reference.

Principles of Weed Control. By GILBERT H. AHLGREN, GLENN C. KLINGMAN, AND DALE E. WOLF. John Wiley & Sons, Inc., New York, 1951. Pp. 368, figs. 109. Price \$5.50.

One is impressed by the progress that has been made in recent years in weed control. This well-documented and attractively illustrated book should prove of wide interest and usefulness to a great many persons who are concerned with this problem in terms of research or in practice. The 17 chapters deal with various methods of control but particularly with weed-killing chemicals. The appendix gives the susceptibility of a wide range of plant species to 2, 4-D and some very useful conversion factors. The book fills an important need.

Resources and Policy. Current Issues in Conservation. Edited by LEE S. GREENE AND RENE DEVISME WILLIAMSON. Kallman Publishing Company, Gainesville, Florida. Pp. 168. Price, paper-bound, \$2.

This symposium is reprinted from *The Journal of Politics*, volume 13, no. 3, 1951. It contains eight papers on food and people, world abundance, forestry, TVA, regional development, resource conservation, federal lands, and politics of conservation. The paper on "food and people—a second look at Malthus' principle of population," by Stanley A. Cain, merits special study. This applies also to "TVA—symbol and reality" by Norman Wengert. But many will find "the politics of conservation—an illustration," the most interesting paper of the group, since it deals with the various federal and state agencies having to do with soil conservation and the political aspects of this problem. This is a very illuminating presentation.

THE EDITORS

KEARNEY FOUNDATION ESTABLISHED

✓The University of California has established an endowment of approximately 2¼ million dollars for researches on fundamental chemistry, physics, biology, and hydrology of soils of arid and semiarid regions. Advanced instruction for soil

science students will also be supported by this endowment. The funds were derived from the recent sale of a large vineyard near Fresno, California, that was bequeathed to the University of California in 1906 by the late Theodore Kearney. The endowment will be known as the Kearney Foundation of Soil Science.

A large part of the food supply of the undernourished populations of the world will have to be produced in regions of dry climates, the areas of which total about one third of the land surface of the earth. It is important that the basic principles underlying successful crop production on these areas be thoroughly understood. Sustained researches under a well-planned and coordinated program offer great promise of success. The Kearney Foundation will afford substantial support for such researches.

SOIL SCIENCE

VOLUME 73

March 1952

NUMBER 3

HYDROLYSIS OF PHYTATE PHOSPHORUS IN SOILS

R. H. JACKMAN AND C. A. BLACK

Iowa Agricultural Experiment Station¹

Received for publication July 26, 1951

Previous work by the authors (3) showed that inositol phosphates, or phytates, form compounds of low solubility with such abundant soil constituents as iron, aluminum, calcium, and magnesium. The solubility of the phytates of these metals was found to be lower than that of the corresponding phosphates. This evidence accounts for the results of Bower (1), which showed that when phosphorus in soluble form as the phytate or the inorganic orthophosphate was added to soils, the phytate was more strongly fixed against dilute acid extraction and was less available to plants. For these reasons, it appeared probable that the limited solubility of the soil phytates is responsible for the persistence of a considerable quantity of phytate phosphorus in soils.

In a subsequent investigation (4), the presence of phytase in soils was verified, and a method was developed for measuring phytase activity in soils. This work disclosed the fact that soils may contain enough phytase to hydrolyze phytin at a substantial rate if enough of the latter is present in soluble form. It provided further indication that solubility of soil phytates is of major importance in determining the rate of hydrolysis. The primary objective of the work reported in the present paper was to determine whether soil phytate solubility, soil phytase activity, or both, limit the rate of phytate hydrolysis. A second objective was to learn something of the relative importance of these two factors in the control of soil phytate hydrolysis.

MATERIALS AND METHODS

Six different samples of soil were brought to the laboratory from the field and used without drying, to minimize changes that might occur in the natural phytase activity. Ten-gram samples of each soil were placed in 2-ounce bottles and treated with different amounts of a solution of phytase² or of sodium phytate, prepared

¹ Contribution from the Iowa Agricultural Experiment Station and the U. S. Department of Agriculture. Journal Paper No. J-1980 of the Iowa Agricultural Experiment Station, Ames. The senior author is now at Rukuhia Soil Research Station, Hamilton, New Zealand.

² The phytase solution was prepared as follows: One part of bran was shaken for 1 hour with five parts of water by weight. The liquid was then squeezed out through cheesecloth and centrifuged to remove the remaining sediment. The supernatant liquid was saturated with $(\text{NH}_4)_2\text{SO}_4$, and the flocculent precipitate that appeared was consolidated by centrifugation. The supernatant liquid was discarded, and the precipitate was placed in a Visking bag and dialyzed against water for 12 hours, whereupon the precipitate dispersed and a clear solution was produced. The $(\text{NH}_4)_2\text{SO}_4$ precipitation and dialysis were repeated. The

according to the procedure described previously (3), plus 0.5 ml. of toluene and enough water to bring the total volume of aqueous reagents to 20 ml. The sodium phytate solution was adjusted to the pH of the soil before addition, but the phytase solution was used without pH adjustment, since it had essentially no effect on the soil pH. The bottle caps were then screwed on tightly, the contents were mixed, and the bottles were allowed to stand for 85 hours at room temperature. The bottles were then opened and 50 ml. of 4 *N* HCl was added. After 30 minutes, the suspension was filtered, the soil was washed with water, and the filtrate was diluted to 500 ml. Inorganic phosphorus was determined in an aliquot by the method of Dickman and Bray (2). In calculating the amount of HCl-solu-

TABLE 1

HCl-soluble inorganic phosphorus in soil samples after 85 hours' incubation at room temperature in presence of toluene and different amounts of sodium phytate and phytase

Based on 10-gm. soil sample

PHYTATE P ADDED	PHYTASE SOLUTION ADDED	HCl-SOLUBLE INORGANIC PHOSPHORUS CONTENT					
		Edina silt loam, pH 5.0	Clarion loam, pH 7.5	Carrington silt loam, pH 5.2	Carrington silt loam,* pH 4.9	Carrington silt loam,* pH 5.4	Carrington silt loam,* pH 6.2
mgm.	ml.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
0	0	0.46	1.31	0.47	0.95	0.83	0.83
4	0	0.48	1.34	0.49	0.96	0.85	0.84
8	0	0.55	1.42	0.60	1.00	0.86	0.87
12	0	0.62	1.41	0.79	1.05	0.92	0.93
16	0	0.72	1.45	0.99	1.08	1.03	0.99
20	0	0.79	1.42	1.07	1.29	1.10	1.03
0	2	0.44	1.28	0.45	0.94	0.81	0.84
0	4	0.47	1.28	0.46	0.94	0.83	0.84
0	6	0.47	1.27	0.46	0.93	0.80	0.83
0	8	0.47	1.25	0.47	0.98	0.83	0.85
0	10	0.47	1.29	0.47	0.94	0.86	0.82

* From field plots treated with different amounts of limestone.

ble inorganic phosphorus in the soil, correction was made for the inorganic phosphorus introduced in the sodium phytate.

RESULTS AND DISCUSSIONS

The results obtained with the individual soil samples are given in table 1. The average results with the six soil samples are plotted in figure 1. It is evident from figure 1 that the hydrolysis increased with the amount of sodium phytate added. These results show that the phytase in the soil was capable of hydrolyzing an appreciable quantity of phytate phosphorus if enough of the latter was present.

According to the theory of Michaelis and Menten (5), the rate of hydrolysis of clear, slightly colored solution obtained in this manner was kept in the refrigerator with toluene for subsequent use. This preparation was superior to that obtained by the alcohol precipitation technique (4) in that the phytase activity was greater and filterable material was absent.

phytate phosphorus as a function of phytate concentration at constant phytase concentration may be expressed by the equation

$$v_p = \frac{V_p P}{P + K_p}$$

where v_p is the reaction velocity obtained with the molar concentration P of the phytate, V_p is the limiting reaction velocity obtainable with excess phytate, and the constant K_p corresponds to that phytate concentration at which half the limiting velocity is developed. It may be inferred from this equation that any limitation imposed by the soil on the solubility of phytate phosphorus will decrease the rate of hydrolysis, v_p , provided the amount in solution is less than that required to produce the maximum rate of hydrolysis, V_p . The fact that addition

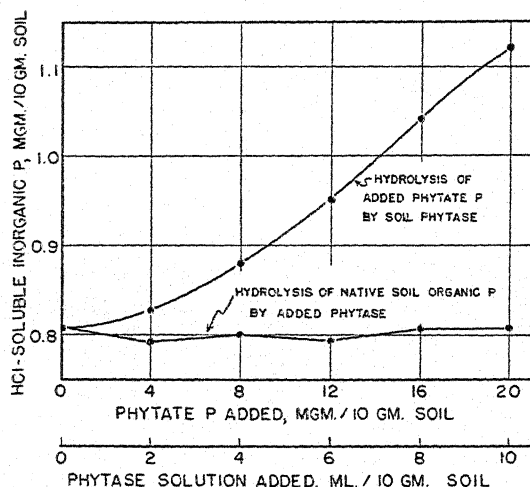


FIG. 1. AVERAGE HCl-SOLUBLE INORGANIC PHOSPHORUS IN SOIL SAMPLES AFTER 85 HOURS' INCUBATION AT ROOM TEMPERATURE IN PRESENCE OF TOLUENE AND DIFFERENT AMOUNTS OF SODIUM PHYTATE AND PHYTASE.

of sodium phytate increased the hydrolysis shows that in the soils investigated the maximum rate of hydrolysis with the existing phytase concentration was not attained with the amount of soil phytate in solution. Since only a minute quantity of the native soil organic phosphorus is found in solution (6), it may be concluded that the solubility of the native soil phytate limited the rate of hydrolysis.

The Michaelis and Menten (5) equation may also be written

$$v_e = \frac{V_e E}{E + K_e}$$

where v_e is the reaction velocity obtained with the molar concentration E of phytase, V_e is the limiting reaction velocity obtainable with excess phytase, and the constant K_e corresponds to that phytase concentration at which half the limiting velocity is developed. This equation expresses the reaction velocity as a

function of phytase concentration at constant phytate concentration. It may be inferred from the equation that any increase in phytase concentration in the soil will increase the rate of phytate hydrolysis, provided the initial concentration of phytase is below that required to produce the limiting reaction velocity.

Figure 1 shows that addition of phytase to the soils did not increase the rate of hydrolysis of the native soil organic phosphorus. There are at least three possible interpretations of this behavior. First, the quantity of phytase initially present in the soils may have been sufficient to produce the limiting reaction velocity with the phytate concentration present. Second, the concentrations of both phytase and phytate may have been low and the increase in hydrolysis produced by the added phytase within the experimental errors of measurement. Third, the added phytase may have been inactivated through contact with the soil.

The third possibility was checked in a separate experiment. Samples of soil were treated with sodium phytate alone and with sodium phytate plus phytase. After 4 days' incubation at room temperature in the presence of toluene, the increase in HCl-soluble inorganic phosphorus was determined as before. It was found that the increase in inorganic phosphorus was five times greater in the presence of added phytase than in its absence. These results show that the activity of the added phytase was not destroyed in presence of soil. Lack of hydrolysis of native soil organic phosphorus apparently was not caused by inactivation of the added phytase. The third possibility may thus be discounted.

Although the experiment shows also that addition of phytase increased the hydrolysis of added phytate phosphorus, it may not be concluded that the quantity of phytase initially present in the soil was insufficient to produce the limiting reaction velocity, since the phytate concentration was much higher than that originally present in the soil. Without additional information it is impossible to distinguish between the possibility that only the solubility of soil phytate operated as a limiting factor and the possibility that both the solubility of soil phytate and the activity of soil phytase acted as limiting factors. An estimate of the relative importance of phytate solubility and phytase activity can, however, be obtained from figure 1.

The relative importance of phytate concentration and phytase activity as limiting factors in the hydrolysis of soil phytate is given by the ratio

$$\frac{V_p - v_p}{V_e - v_e}$$

where the symbols have the meaning already assigned. It appears from figure 1 that V_p is about 0.5 mgm. of phosphorus per 10 gm. of soil and that V_e is 0. Neither v_p nor v_e is known, but $v_p < V_p$, $v_e < V_e$, and in the controls, where neither phytase nor phytate was added, $v_p = v_e$. If the values $V_p = 0.5$ and $V_e = 0$ are then substituted in the above expression, it is evident that phytate solubility is of infinitely greater importance than phytase activity. If it is assumed, however, that in the experiment the difference between V_e and v_e was finite but within experimental error, the ratio will have some finite value. The average increase in HCl-soluble inorganic phosphorus in the five phytase-treated samples

was -0.007 mgm. with fiducial limits of ± 0.014 mgm. at the 95 per cent level of probability. If the upper limit is taken for purposes of calculation, the relative importance of phytate solubility and phytase activity is given by the ratio

$$\frac{0.5 - v_p}{0.007 - v_e}$$

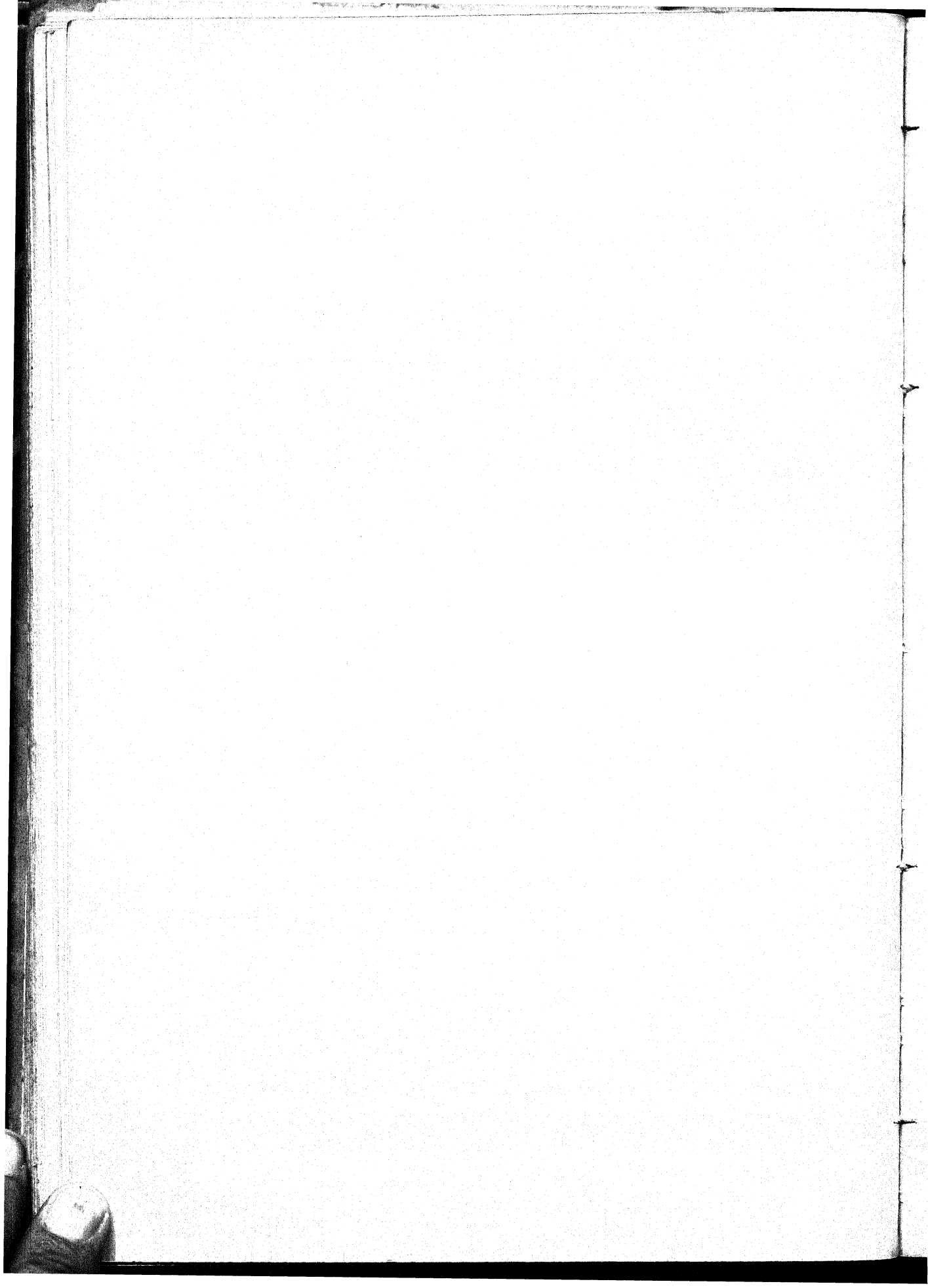
If it is now assumed that $v_e = 0$, the probability is thus 95 per cent that phytate solubility was more than 71 times as important as phytase activity in limiting the rate of hydrolysis of the soil phytate phosphorus.

SUMMARY

The hydrolysis of native soil organic phosphorus by added phytase and the hydrolysis of added phytate phosphorus by soil phytase were determined on six samples of soils brought from the field and tested without previous drying. There was substantial hydrolysis of added phytate phosphorus by soil phytase, but there was no detectable hydrolysis of soil organic phosphorus by added phytase. The limited amount of phytate phosphorus in solution in the soils was thus a deterrent to rapid hydrolysis of soil phytate phosphorus. Either the amount of phytase present was adequate to produce the maximum hydrolysis rate of soil phytate phosphorus or the increase in hydrolysis rate produced by the added phytase was within the experimental error of measurement. Application of the Michaelis and Menten theory of enzyme action to the data made possible the estimate that the amount of soil phytate phosphorus in solution was at least 71 times as important as the phytase activity in limiting the hydrolysis rate of soil phytate phosphorus.

REFERENCES

- (1) BOWER, C. A. 1949 Studies on the forms and availability of soil organic phosphorus. Iowa Agr. Exp. Sta. Res. Bul. 362.
- (2) DICKMAN, S. R., AND BRAY, R. H. 1940 Colorimetric determination of phosphate. *Indus. and Engin. Chem., Analyt. Ed.* 12: 665-668.
- (3) JACKMAN, R. H., AND BLACK, C. A. 1951 Solubility of iron, aluminum, calcium, and magnesium inositol phosphates at different pH values. *Soil Sci.* 72: 179-186.
- (4) JACKMAN, R. H., AND BLACK, C. A. 1952 Phytase activity in soils. *Soil Sci.* 73: 117-125.
- (5) MICHAELIS, L., AND MENTEN, M. L. 1913 Die Kinetik der Invertinwirkung. *Biochem. Ztschr.* 49: 333-369.
- (6) PIERRE, W. H., AND PARKER, F. W. 1927 Soil phosphorus studies: II. *Soil Sci.* 24: 119-128.



EFFECT OF ORGANIC MATTER ON PHOSPHATE AVAILABILITY

JOSEPH D. DALTON, GLENN C. RUSSELL, AND DALE H. SIELING

Massachusetts Agricultural Experiment Station¹

Received for publication August 3, 1951

Many investigations, extending over the last 80 years, have shown that only 10 to 20 per cent of applied phosphate is utilized by crops, and the rest is fixed in a form not readily available. Recent investigations with radio phosphorus at several locations and with several crops have confirmed previous observations and have shown also that plants obtain an unusually high proportion of phosphate from that already present in the soil (4).

The process of phosphate fixation has received considerable attention, and many theories have been advanced to explain it. The experimental results of Bass and Sieling (2), Bear and Toth (3), Cole and Jackson (7), Coleman (8), Ford (12), Haseman *et al.* (15), and many others (6, 13, 16, 19, 20, 22, 23, 27) indicate that specific compounds of iron and aluminum, which are relatively insoluble, are formed when soluble phosphates are added to acid soils. These compounds have been identified recently by Cole and Jackson (7) as ferric dihydroxyl dihydrogen phosphate (*strengite*) and aluminum dihydroxyl dihydrogen phosphate (*variscite*) or isomorphous combinations of the two (*barrandite*).

Many investigators (1, 9, 14, 17, 20) observed that organic matter increased the availability of soil phosphate and of rock phosphate which was added to the soil as fertilizer. Bradley,² Struthers and Sieling (26), and Swenson *et al.* (27) have shown that many organic substances commonly found in soils are very effective in preventing the precipitation of phosphate *in vitro* by iron and aluminum between pH values of 3 to 9. Leclerc³ has also pointed out that the various fixed phosphate substances are readily dissolved by the action of these same organic substances.

The purpose of this investigation was to determine by plant uptake the relative availability of the phosphate precipitated by iron and aluminum under acid conditions and to determine the effectiveness of organic matter in making available to plants the phosphate fixed in acid soils or contained in rock phosphate.

EXPERIMENTAL

Precipitated phosphates as sources of phosphate for plants

The principal products of phosphate fixation in acid soils formed by the reactions of soluble phosphate with iron and aluminum compounds are relatively

¹ Contribution No. 810, Massachusetts Agricultural Experiment Station, Amherst.

² Bradley, D. B. Precipitation of phosphorus by iron and aluminum as influenced by pH and pure organic substances. 1951. [Unpublished master's thesis. Copy on file University of Massachusetts Library, Amherst.]

³ Leclerc, J. L. Solubilization effect of citric acid on some insoluble phosphate salts. 1951. [Unpublished master's thesis. Copy on file University of Massachusetts Library, Amherst.]

insoluble and are, therefore, believed to be poor sources of phosphate for growing plants. It is known, however, that certain organic substances, particularly hydroxyorganic acids, normally produced in soils by action of microorganisms, are effective in dissolving these phosphate fixation substances by forming stable complex molecules with the iron and aluminum. Would this dissolving action on precipitated phosphate be sufficiently great to be reflected in increased plant growth or phosphate absorption by plants or both?

A fixed phosphate substance containing iron was prepared by the method of Swenson *et al.* (27). Ferric chloride solution was mixed with soluble phosphate in a strongly acid solution containing about 1 per cent NaCl. The mixture was boiled, and NaOH was added to adjust the pH value to 5.5; the boiling was then continued for $\frac{1}{2}$ hour. The precipitated "iron phosphate" was washed thoroughly to remove the adsorbed phosphate. The fixed phosphate substance was believed to be a mixture of ferric dihydroxyl dihydrogen phosphate and hydrated ferric oxide because it was formed at a more alkaline reaction than is required for maximum precipitation of phosphate by iron (27). A similar procedure was followed to prepare a fixed phosphate substance of aluminum. Both precipitates were maintained in a moist state to avoid any decrease in availability that might result from excessive drying. The moist precipitates containing 4 per cent phosphorus were completely soluble in citric acid, and portions of the precipitates that were dried in the laboratory for 18 months were also completely soluble in this reagent. Both precipitates were only slightly soluble in boiling distilled water.

These fixed phosphate substances were used in various quantities as sources of phosphate for plants grown in sand cultures. Other essential elements were added as a modified Knop's solution (21) from which the soluble phosphate was omitted. Complete Knop's solution was used for comparative cultures. The fixed phosphate substances were mixed thoroughly with the clean sea sand prior to planting. After seeding, the appropriate solutions were added periodically to maintain optimum moisture conditions and until the desired total quantity of nutrients had been added to each culture. Sodium citrate was incorporated in the nutrient solution as a source of organic substance for part of the cultures. Subsequently, the cultures were kept moist with distilled water.

The fixed phosphate substances added to the different cultures contained phosphate in amounts approximately equal to 13 and 26 times that present in the cultures receiving soluble phosphate. Separate sets of cultures, each containing the smallest quantity of each of the fixed phosphate substances, received sodium citrate in addition to the regular essential nutrients.

Six seeds of a selected inbred line of popcorn were planted in each prepared sand culture. All cultures were grown in duplicate. After germination, the seedlings were thinned to leave the three most vigorous plants. All plants were harvested just as the tassels were beginning to appear. Yield of each culture was calculated on dry weight basis, and phosphorus was determined by modification of the method of Sherman (24). The phosphorus uptake of the test plants grown in these cultures is represented in figure 1.

These data indicate that the precipitated and thoroughly washed fixed phos-

phate substances of iron and aluminum have limited phosphate-supplying ability. The plants obtained only about one-seventh as much phosphate from the two insoluble substances as from the soluble form when approximately equal quantities were present; however, when the insoluble substances were present in manifold quantities, the uptake of phosphate was about equal to that of the plants grown in the cultures containing soluble phosphate. Where large quantities of these

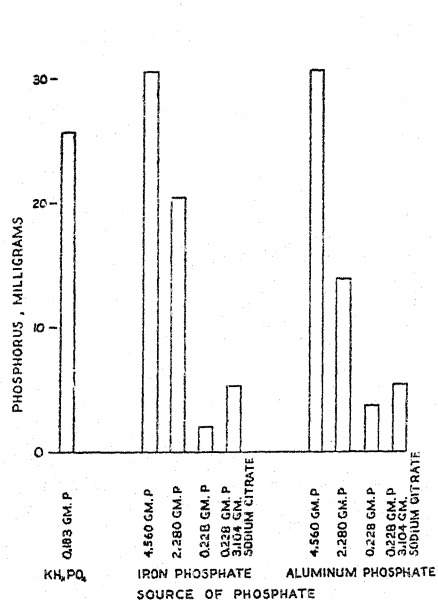


FIG. 1

FIG. 1. EFFECT OF QUANTITY OF FIXED PHOSPHATE SUBSTANCES AND OF ORGANIC MATTER ON UPTAKE OF PHOSPHATE BY PLANTS

Iron phosphate = mixture of ferric dihydroxyl dihydrogen phosphate and hydrated ferric oxide but not FePO_4 ; aluminum phosphate = mixture of aluminum dihydroxyl dihydrogen phosphate and hydrated aluminum oxide but not AlPO_4 .

FIG. 2. EFFECT OF ORGANIC MATTER AND PHOSPHATE FERTILIZATION ON UPTAKE OF PHOSPHATE BY CORN

Phosphate uptake represents sum of three cultures. Spent hops contained 0.24 per cent phosphorus. Organic matter and KH_2PO_4 : ■ hops and KH_2PO_4 applied separately; □ hops and KH_2PO_4 mixed before application.

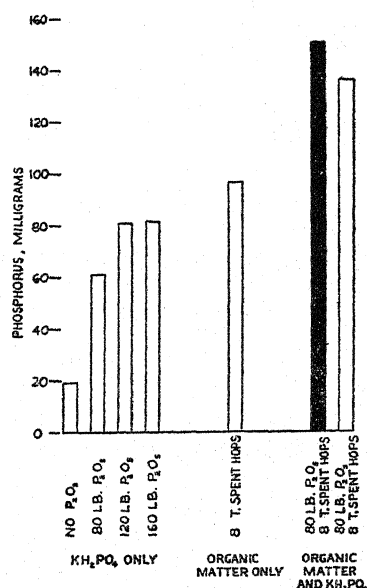


FIG. 2

fixed phosphate substances are present the slight degree of availability is probably overcome by the gross quantitative effect resulting from the greater root-mineral contact. Gerretsen (14) showed that insoluble phosphates were solubilized in the rhizosphere, either by the action of microorganisms or through the action of plant root exudates. The influence of the citrate treatment was slight, but there was a positive effect indicating the need for further investigation to determine the value of organic matter in making insoluble fixed phosphate available to plants.

Effect of organic matter on availability of soil phosphate

Dean and Rubins (10), Kurtz *et al.* (18), and others (2, 5, 11) have observed that certain organic anions are effective in extracting phosphate from soils. According to Waksman and Reuszer (29) and others (26, 30), the most effective of these, citrate, oxalate, tartrate, and many less effective organic substances are commonly produced in soils by the action of microorganisms. Jensen (17) reported that water extracts of decomposing organic matter were one to five times more effective than water alone in dissolving phosphate from soils. The uptake of phosphate by crops from plots treated with manure was greater than from unmanured plots, although the total phosphate present was the same, according to Copeland and Merkle (9). Midgley and Dunklee (20) found that manure increased markedly the availability of phosphate, especially when the phosphate and manure were mixed prior to application.

Organic matter containing phosphorus. In a preliminary experiment, spent brewers' hops, which contained 0.24 per cent total phosphorus, none of which was water-soluble, were used as a source of organic matter to determine whether fixed phosphate could be made available to plants through the action of microorganic decomposition of organic matter. A soil known to have a high phosphate-fixing capacity and to be low in available phosphate was used for duplicate pot cultures representing each treatment. For each replicate 25 pounds of soil was used. All cultures received uniform treatments of calcium, potassium, magnesium, and nitrogen, but rates of phosphate fertilization and applications of organic matter varied: one set of duplicates received no phosphate or organic matter; three sets received soluble inorganic phosphate at rates of 80, 120, and 160 pounds of P_2O_5 per acre, respectively; one set received spent hops equivalent to 80 pounds of P_2O_5 per acre (an application of 8 tons per acre is equivalent to 80 pounds of P_2O_5); one set received spent hops equivalent to 80 pounds of P_2O_5 per acre into which was mixed soluble inorganic phosphate equal to an 80-pound P_2O_5 application; and another set was treated like the previous one, except the hops and inorganic phosphate were added to the soil separately.

Four plants of an inbred line of corn, Massachusetts 121A, were grown in each pot and were harvested just as the tassels were appearing. Dry matter was determined, and the samples were analyzed for phosphorus. The various treatments and the resulting phosphorus uptake by corn plants resulting therefrom are represented in figure 2.

These data indicate that crops grown on this treated soil respond to phosphate fertilization, but the most striking effect was produced by the addition of organic matter. An application of 80 pounds of P_2O_5 as soluble phosphate trebled the phosphorus uptake by the test crops, but organic matter containing the same quantity of water-insoluble phosphate increased the uptake fivefold in comparison with that of the untreated culture. The increased uptake of phosphorus from an application of 160 pounds of soluble P_2O_5 per acre was almost four times the uptake of the untreated culture but was only about half the increased uptake resulting from the combination treatment of spent hops and inorganic phosphate, which together contained phosphorus equivalent to the 160-pound rate.

Since the spent hops contained organically combined phosphorus, it is possible that the increased phosphorus uptake by the test plants may have been caused by the slow but constant mineralization of this phosphorus by microorganisms. Even if this were the case, the phosphate thus mineralized or that added as inorganic fertilizer was prevented from being fixed in the soil to the same degree as the inorganic fertilizer that had been added without supplemental organic matter.

Organic matter containing no phosphorus. The proof that the substances formed by microbiological decomposition of organic matter are effective in freeing fixed phosphate would depend upon the use of pure organic substances containing no phosphorus but serving as substrate for the growth of the organisms. Carbohydrate substances are energy sources for a wide number of soil microorganisms which produce a considerable assortment of organic acids as a result of metabolic processes. Many of the acids produced are those most effective in preventing precipitation of phosphate as insoluble substances with iron and aluminum under acid conditions *in vitro*.

The effect of organic matter on the availability of the phosphate in rock phosphate has been the subject of numerous investigations. Bauer (1) found increased phosphate uptake where mixtures of organic matter and rock phosphate were added to soils. Gerretsen (14) found that the action of microorganisms increased the availability of the phosphate in rock phosphate, whereas Waksman (30) reported an increase in the solubility of rock phosphate as a result of the action of certain constituents of humus.

This experiment was designed to determine the effect of organic matter on the availability of fixed phosphate and of the phosphate of rock phosphate. Starch, sucrose, glucose, and citrus pectin were chosen as the organic substances because they contain insignificant amounts of phosphorus; are normally found in plant residues; and are metabolized by soil microorganisms to produce such organic acids as citric, oxalic, tartaric, malic, malonic, and galacturonic, all of which have been shown to be effective in replacing fixed phosphate (26). The test soil, Merrimac fine sandy loam, low in available phosphate and with a relatively high fixing capacity, contained 2.62 millimols of citrate-extractable phosphate per 100 gm., and had a pH value of 5.2.

Each culture consisted of 25 pounds of the test soil in 3-gallon glazed porcelain jars. Each treatment was replicated three times. The various fertilizers and organic substances were thoroughly mixed with the soil. Calcium and magnesium were added as nitrates; potassium was added as chloride; soluble phosphate, as KH_2PO_4 ; and some cultures received ground Florida rock phosphate.

Corn was grown in these cultures from June to August until it reached the tasseling stage. It was then harvested by cutting just above the bracer roots, and the plants were dried, ground, and analyzed for phosphorus. The uptake of phosphorus was calculated from the composition and dry-weight production. The various treatments and the resulting phosphate uptake are represented in figure 3.

These data indicate a striking response of the corn to fertilization with soluble phosphate; a slight response to some of the organic matter applications; and a

slight response to rock phosphate fertilization. The soluble and easily decomposable sucrose and glucose had the greatest effect of any of the organic substances with both the soil and rock phosphate sources.

Since the effects of the organic substances were variable and not particularly great for this relatively fast growing corn crop, it was decided to use the same soils for the growth of ladino clover, a more slowly growing crop requiring high phosphate. Additional quantities of starch and pectin were incorporated in the soil in preparation for planting. The sucrose and glucose were added periodically as solutions at $\frac{1}{2}$ - or 1-ton rates per acre over a period of 20 weeks. The plants

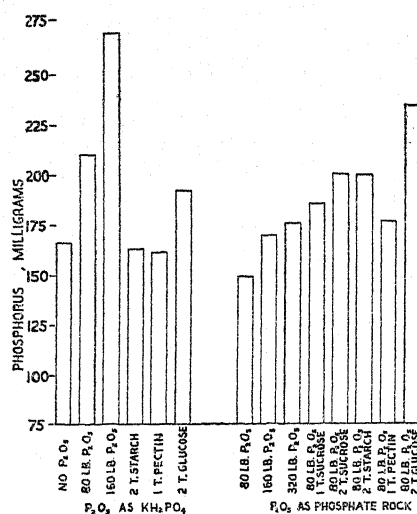


FIG. 3

FIG. 3. EFFECT OF PHOSPHATE FERTILIZATION AND OF ORGANIC MATTER ON UPTAKE OF PHOSPHATE BY CORN

Uptake represents sum of three cultures.

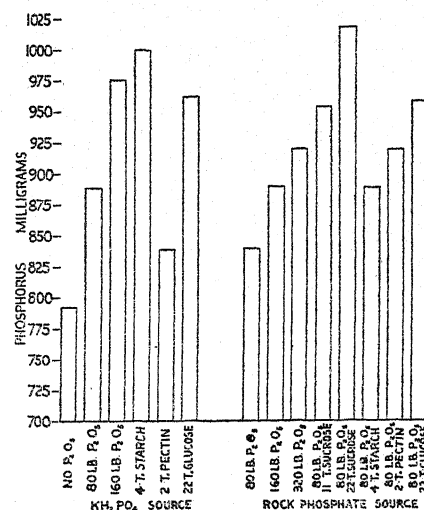


FIG. 4

FIG. 4. CUMULATIVE PHOSPHATE UPTAKE OF SIX CUTTINGS OF LADINO CLOVER AND ONE CORN CROP AS AFFECTED BY FERTILIZATION AND ORGANIC MATTER

Uptake represents sum of three replicates.

were forced to accentuate the phosphate requirements by supplemental periodic additions of calcium, potassium, magnesium, nitrogen, and borax.

To eliminate genetic differences between plants in the various replicates and different cultures, enough stolons were obtained from a single parent plant to allow one stolon for each individual pot culture. Eight stolons from eight different parent plants were planted in each pot. The plant material was cut from the ladino clover for analysis every 6 weeks for 30 weeks. Thereafter, the cuttings were every 3 weeks, and composites of two successive cuttings were made to represent one 6-week growth period—a necessary procedure because of greater growth during summer. The total growth period for the ladino clover was 42 weeks. All cuttings were dried immediately, weighed, prepared for analysis, and

analyzed. Total phosphorus uptake for the ladino clover crops was added to the phosphorus uptake of the corn grown in the same pot. The cumulative uptake of phosphorus is represented graphically in figure 4 for the two crops, corn and ladino clover, along with the phosphate and organic matter treatments.

These data indicate that when organic substances containing almost no phosphate are added to the soil, they have the same effect in increasing phosphate uptake by plants as does the soluble phosphate in the soil which resulted from phosphate fertilization. There was considerable variation in the magnitude of the effect, but in all cases it was positive and in two cases was about the same as the increase caused by a 160-pound P_2O_5 application of soluble phosphate. All treatments of organic substance, except a combination of rock phosphate and starch, caused a gradual increase in the phosphate uptake with each harvest. The starch-rock-phosphate combination resulted in a definite increase in phosphate uptake by the plants through the second cutting of ladino clover. In successive cuttings thereafter there was a gradual decrease; the net cumulative results for the seven cuttings were only slightly greater than for the cultures receiving only the rock phosphate and considerably less than for those receiving only the starch. The reason for this anomaly is not apparent to the authors.

The increased uptake of phosphorus resulting from the various rock phosphate treatments indicated that this material was an effective source of phosphate but was somewhat less efficient than the soluble phosphate. The 160 pounds of P_2O_5 from rock phosphate gave approximately the same phosphate uptake as the 80 pounds of P_2O_5 from soluble phosphate. The gross effect of organic matter in combination with rock phosphate was greater than that from rock phosphate alone; however, the increased uptake of phosphate from the combination could not be specifically attributed to an effect of the organic matter on the rock phosphate because the increase was no greater than that produced by the organic matter alone. It seems logical to propose, however, that since both organic matter and rock phosphate gave increases when used alone, the increase resulting from their use together was contributed by both materials, and that over a long period this combination would be more effective than either material by itself.

DISCUSSION

In addition to the many beneficial effects previously attributed to soil organic matter, we can now add that of making soil phosphorus more available. Practical farmers have long known that as soil organic matter decreased, there was also a parallel increase in the phosphate requirement for high production of crops. Several investigators (1, 9, 14, 17, 20, 28, 30) have reported that phosphate added to the soil with organic matter has greater availability than the same amount of phosphate added without organic matter. The results of previous investigations indicate that certain organic substances, principally the hydroxyorganic acids and other substances particularly effective in forming stable complex molecules with iron and aluminum, would effect liberation of fixed phosphate (18, 26, 27). These organic compounds are the very substances that are formed as a result of the microorganic oxidation of carbohydrate materials in soils—tartaric acid,

oxalic acid, citric acid, malic acid, malonic acid, galacturonic acid, and many others (25, 28, 30).

Possibly this is nature's way of preventing reduction of phosphate to such a low level of availability that plants would not be able to grow. The intensive activity of microorganisms in the rhizosphere may well be the factor that makes the insoluble phosphate available for plant use. Certain organic energy substances exuded by plant roots could serve as the raw materials from which the microorganisms produce the necessary phosphate liberators. Gerretsen (14) found that the phosphate absorbed from insoluble minerals by plants grown in sterile cultures was very small in comparison with phosphate absorption from identical cultures containing microorganisms.

These experiments point out that readily decomposable organic matter has about the same net effect on plant growth and phosphate uptake as has phosphate fertilization of a soil low in available phosphate. The active agents that make the phosphate available are believed to be organic substances produced by microbiological action and particularly effective in forming stable complex molecules with iron and aluminum.

SUMMARY AND CONCLUSIONS

Organic matter added to the soil as an amendment is effective in increasing the availability of soil phosphate. Easily decomposable organic matter is more effective in this regard than are organic substances that decompose slowly.

The fixation products of phosphate with iron and aluminum are relatively poor sources of phosphate for plants.

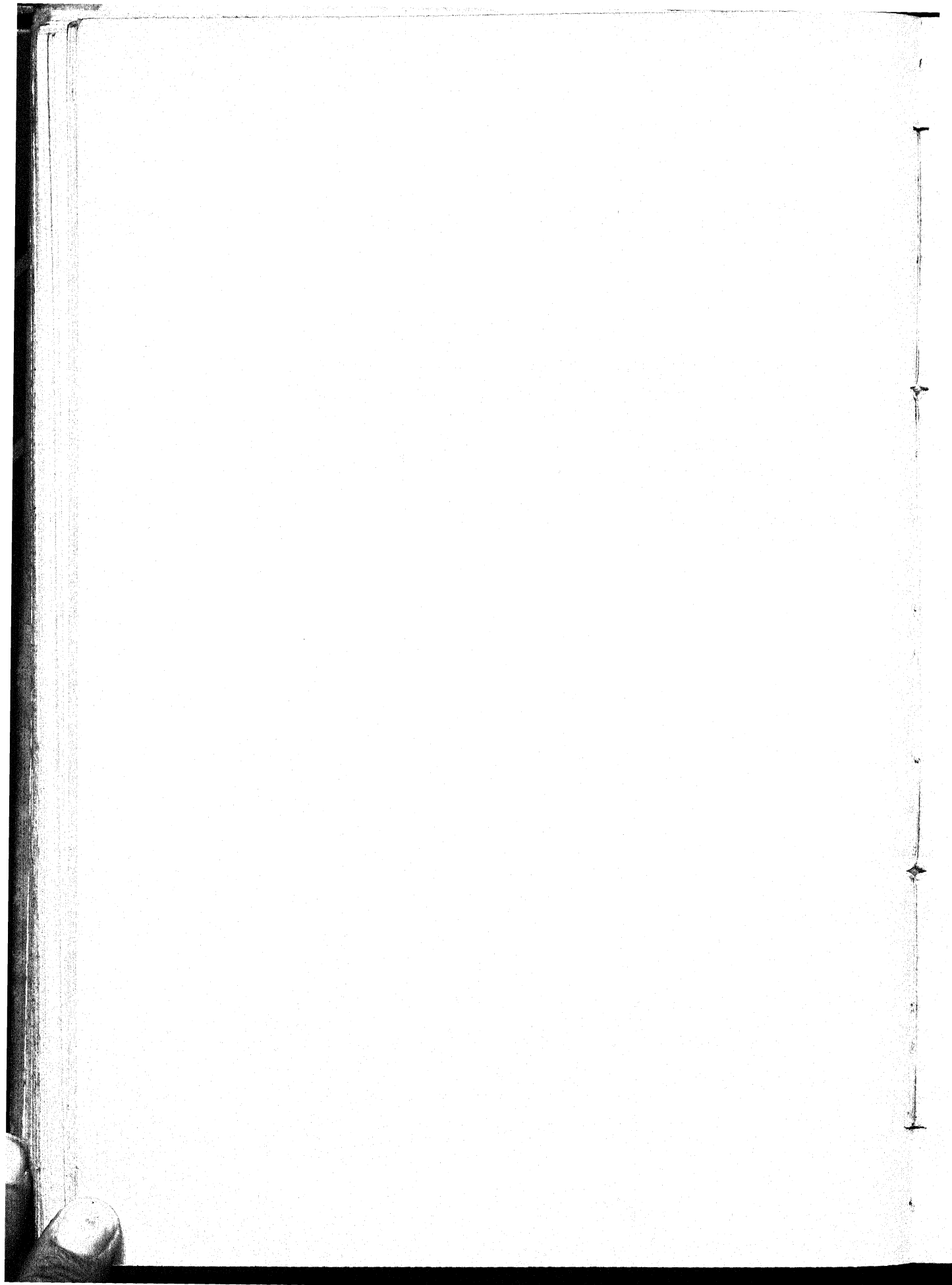
Rock phosphate served as a very good source of phosphate for ladino clover but was less efficient than soluble phosphate. The efficiency of the rock phosphate was increased by the presence of sucrose, glucose, and pectin but not by starch.

The activity of the organic matter in making soil phosphate available is attributed to the ability of certain metabolic products of microbiological decomposition to form stable complex molecules with the iron and aluminum that are responsible for phosphate fixation in acid soils.

REFERENCES

- (1) BAUER, F. C. 1921 Relation of organic matter and feeding power of plants to utilization of rock phosphate. *Soil Sci.* 12: 21-41.
- (2) BASS, G. B., AND SIELING, D. H. 1950 Method for determining relative phosphate-fixing capacity of acid soils. *Soil Sci.* 69: 269-280.
- (3) BEAR, F. E., AND TOTH, S. J. 1942 Phosphate fixation in soil and its practical control. *Indus. and Engin. Chem.* 34: 49-52.
- (4) BEAR, F. E. (Editor) 1949 Utilization of phosphorus by various crops through the use of radiophosphorus. *Symposium on phosphate utilization. Soil Sci.* 68: 113-202.
- (5) BRAY, R. H., AND DICKMAN, S. R. 1942 Adsorbed phosphates in soils and their relation to crop responses. *Soil Sci. Soc. Amer. Proc.* (1941) 6: 312-320.
- (6) BROWN, L. A. 1935 Phosphorus penetration and availability in soils. *Soil Sci.* 39: 277-287.
- (7) COLE, C. V., AND JACKSON, M. L. 1951 Solubility equilibrium constant of dihydroxy aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils. *Soil Sci. Soc. Amer. Proc.* (1950) 15: 84-89.

- (8) COLEMAN, R. 1945 Mechanism of phosphate fixation by montmorillonitic and kaolinitic clays. *Soil Sci. Soc. Amer. Proc.* (1944) 9: 72-78.
- (9) COPELAND, O. L., AND MERKLE, F. G. 1942 Influence of certain soil treatments upon the fixation and availability of applied phosphates. *Soil Sci. Soc. Amer. Proc.* (1941) 6: 321-327.
- (10) DEAN, L. A., AND RUBINS, E. G. 1947 Anion exchange in soils: I. *Soil Sci.* 63: 377-387.
- (11) DICKMAN, S. R., AND BRAY, R. H. 1941 Replacement of adsorbed phosphate from kaolinite by fluoride. *Soil Sci.* 52: 263-273.
- (12) FORD, M. C. 1933 Nature of phosphate fixation in soils. *Jour. Amer. Soc. Agron.* 25: 134-144.
- (13) FRAPS, G. S. 1922 Fixation of phosphoric acid by the soil. *Tex. Agr. Exp. Sta. Bul.* 304.
- (14) GERRETSEN, F. C. 1948 Influence of microorganisms on the phosphate intake by the plant. *Plant and Soil* 1: 51-81.
- (15) HASEMAN, J. F., BROWN, E. H., AND WHITT, C. D. 1950 Some reactions of phosphate with clays and hydrous oxides of iron and aluminum. *Soil Sci.* 70: 257-271.
- (16) HECK, A. F. 1934 Phosphate fixation and penetration in soils. *Soil Sci.* 37: 343-355.
- (17) JENSEN, C. A. 1917 Effect of decomposing organic matter on the solubility of certain inorganic constituents of the soil. *Jour. Agr. Res.* 9: 253-268.
- (18) KURTZ, T., DETURK, E. E., AND BRAY, R. H. 1946 Phosphate adsorption by Illinois soils. *Soil Sci.* 61: 111-124.
- (19) METZGER, W. H. 1941 Phosphorus fixation in relation to the iron and aluminum of the soil. *Jour. Amer. Soc. Agron.* 33: 1093-1099.
- (20) MIDGLEY, A. R., AND DUNKLEE, D. E. 1945 Availability to plants of phosphates applied with cattle manure. *Vt. Agr. Exp. Sta. Bul.* 525.
- (21) MILLER, E. C. 1938 *Plant Physiology*. McGraw-Hill Book Company, Inc., New York and London.
- (22) PERKINS, A. T., AND KING, H. H. 1944 Phosphate fixation by soil minerals: II. *Soil Sci.* 58: 243-250.
- (23) PERKINS, A. T. 1948 Phosphate solubility in relation to cations and pH: Magnesium. *Soil Sci. Soc. Amer. Proc.* (1947) 12: 185-187.
- (24) SHERMAN, M. S. 1942 Colorimetric determination of phosphorus in soils. *Indus. and Engin. Chem., Analyt. Ed.* 14: 182-185.
- (25) SHOREY, E. C. 1913 Some organic soil constituents. U. S. Dept. Agr. Bur. Soils Bul. 88.
- (26) STRUTHERS, P. H., AND SIELING, D. H. 1950 Effect of organic anions on phosphate precipitation by iron and aluminum as influenced by pH. *Soil Sci.* 69: 205-213.
- (27) SWENSON, R. M., COLE, C. V., AND SIELING, D. H. 1949 Fixation of phosphate by iron and aluminum and replacement by organic and inorganic ions. *Soil Sci.* 67: 3-22.
- (28) WAKSMAN, S. A., AND STARKEY, R. L. 1931 *Soil and the Microbe*. John Wiley and Sons, Inc., New York.
- (29) WAKSMAN, S. A., AND REUSZER, H. W. 1932 Origin of the uronic acids in humus of soil, peat, and composts. *Soil Sci.* 33: 135-151.
- (30) WAKSMAN, S. A. 1938 *Humus*. The Williams and Wilkins Co., Baltimore.



SOME CHARACTERISTICS OF THE MACROSTRUCTURE OF TROPICAL SOILS IN PUERTO RICO

R. M. SMITH AND C. F. CERNUDA

U. S. Department of Agriculture¹

Received for publication August 16, 1951

In studying the macrostructure of Puerto Rican soils, we have used both observational and laboratory testing methods. Some of our successful laboratory evaluations have involved air-slaking and resistance to known energy applications from falling water drops (8). This kind of testing appears to be most useful when applied to aggregates selected to represent particular soil-type horizons or conditions reflecting soil treatment or use. With well-correlated tests there is a chance of learning to recognize and to take advantage of features of aggregates that give consistent indications of stability.

Besides aggregate stability relations, other features of soil structure must be described accurately to enable one to predict such phenomena as erodibility, water movement, aeration, and associated fertility features of soil profiles. O'Neal (4) has shown that subsoil permeability can be estimated when the proper clues are observed and evaluated. Schuylenborgh (6) has been making outstanding progress in relating structural observations to water and air supplies and to productivity. He considers that ideal units should be both highly porous and firm. Bradfield (2) recently emphasized the importance of structure to increased world production of crops and indicated some of the probable relations of colloidal reactions and root growth to the desirable physical conditions recognized as basic in successful farm practice. There appear to be many examples of the need for improved observations and descriptions of structure to help clarify both practical and theoretical problems. Excellent technical information related to soil structure may be misleading unless it is rather definitely correlated with observations and descriptions of desired field conditions. Technical interpretations that conflict with practical observations of desirable physical conditions may reflect weaknesses in the laboratory methods of evaluation.

A descriptive approach to soil structure is dependent upon accurate perception, clear concepts, and adequate terminology. To qualify as adequate, the terminology needs to describe structural conditions to the satisfaction of the observer. At the same time it should serve to convey an accurate picture to others. Regardless of how well an individual likes certain words, he cannot escape the fact that their scientific value depends upon their interpretations by others. On the other hand, little is gained by accepting or being bound by terminology which restricts the observer's concepts. It appears best for the present purpose to avoid ques-

¹ Report on the cooperative project "Erosion control and stable crop production in Puerto Rico" of the Puerto Rico Agricultural Experiment Station at Rio Piedras and the U. S. Department of Agriculture. For suggestions and cooperation in developing and testing the terminology used in this paper, the authors are grateful to J. A. Bonnet, Juan P. Cordova, Fernando Abruña, Servando Silva, and Jose Vicente-Chandler.

tionable terms altogether, and to describe or give measured values for the various characteristics of aggregates and of structure whenever possible. Such information can always be converted into favored structural terms by any one who wishes to do so.

CHARACTERIZATION OF SOIL STRUCTURE

In expressing our concepts of the typical soil structural conditions in Puerto Rico, we believe that it is necessary to consider the following characteristics of aggregates:²

1. *Distinctness (or Grade)*. We use this term essentially as recommended by the Soil Survey Division of the Bureau of Plant Industry, Soils, and Agricultural Engineering of U. S. Department of Agriculture (3). The distinctness of development of structure is described in a relative sense as weak, moderate, strong, or very strong. If no aggregation is evident, this condition should be indicated as nonaggregated.

2. *Angularity of aggregates*.

- a. Very angular
- b. Subangular
- c. Rounded—no edges

3. *Axial length of aggregates*. Express as average ratio of horizontal to vertical, or as $\frac{H}{V}$.

This appears to provide an adequate expression of shape when angularity has been indicated.

4. *Predominant size*. Size is often difficult to define definitely because many aggregates break into progressively smaller units depending only on the vigor of the handling. Whenever possible, we express the most obvious dimensions in centimeters or millimeters.

5. *Observable internal porosity*. There are no absolute standards to express this accurately. We attempt to use relative terms essentially as done by O'Neal (4) and to define these terms as corresponding to certain predominant pore sizes, as follows:

<i>Porosity Description</i>	<i>Diameter of the Predominant Pores</i>
Coarse	Greater than 0.50 mm.
Medium	0.10 to 0.50 mm.
Fine	0.02 to 0.10 mm.
Very fine (or none)	Less than 0.02 mm.

The "very fine" rating approximates the lower limit of visibility. It is also the pore size below which moisture tension studies have indicated that the contribution to percolation will normally be less than 0.01 inch per hour at unit hydraulic head (7), a very slow rate. When aggregates have coarse internal porosity, percolation rates are almost certain to be high. With fine or very fine internal porosity, the percolation capacity is highly variable, depending on the nature of cleavages and on density of packing of the aggregates.

6. *Stability*. Our use of this term is based at present primarily on laboratory testing of macroaggregates, plus certain confirmatory field observations. The testing conditions must be specified before definite statements are justified; but, in general, our stability tests are intended to approximate common conditions to which surface soil is subjected during use for crop production. Appropriate descriptive terms are: stable, moderately stable, weakly stable, and unstable. Basic tests are slaking in water and destruction by water drops.

² The term *aggregate* refers in an indefinite sense to any kind of structural unit or group of textural particles. This is believed to be consistent with general usage (1). Structural type names are obviously not needed when aggregates are completely described as outlined.

In addition to the character of aggregates themselves, their *arrangement* is important. O'Neal (4) has offered outstanding evidence of the importance of the degree of overlap and the cleavage directions among aggregates. *Overlap* can best be expressed as an estimated percentage. *Direction of cleavages* separating aggregates (used primarily with angular aggregates) is conveniently expressed as: 1. Vertical only (*V*); 2. Horizontal only (*H*); 3. Oblique (*O*). All combinations of these directions are possible. The dominant direction is indicated first; or if none is considered dominant, all are indicated equal, as $V = H = O$.

The *closeness of packing* of aggregates may also be observed and described as dense, medium, and loose. This factor largely determines the number and size of pores among aggregates. Volume weight measurements are a good check on closeness of packing. In Puerto Rico a clay with angular aggregates and $\frac{H}{V} =$ close to 1, will have a volume weight of about 1.0 to 1.2 if loosely packed, 1.2 to 1.4 if medium packed, and 1.4 to 1.6 if densely packed.

Another factor which is related to closeness of packing but which sometimes deserves a separate rating is *cohesion among aggregates*, or crushing strength of the soil mass. We are confident that it is feasible consistently to distinguish weak or very weak cohesion from strong or "normal" cohesion; but we have not attempted to go further than that. The soil moisture content would apparently need to be carefully controlled for finer distinctions.

In all descriptions of soil structure it seems important to note the *soil moisture condition* as closely as possible. We are using the following designations of field moisture: wet (or excess water); essential field capacity; below field capacity (about pF 3, ideal for working the soil); dry; and very dry (at or drier than the wilting point). Some field soil moisture samples are helpful for maintaining a consistent interpretation of moisture relations; and moisture tension or pF curves provide a needed laboratory calibration.

In addition to descriptions of aggregates, it is recognized that some soil materials may show no aggregation. Such conditions are sometimes described as structureless, although we prefer to consider, as does Bradfield (2) that single-grain arrangement is one aspect of structure. Clays without aggregation are often called *massive*. For consistent clarity, the term *nonaggregated* is used in this paper, and *observable internal porosity* is described in the same way as are aggregates. *Texture* and *density* should also be a part of every description of a *nonaggregated* condition.

RESULTS OF AGGREGATE STABILITY MEASUREMENTS

The outstanding fact about aggregate stability revealed by our laboratory tests is the large, consistent difference between surface soils and subsoils of the same profiles. As shown by Table 1, most 1-gm. subsoil aggregates are largely destroyed by air-slaking. When they are not completely destroyed, only a few water drops are required to pass them through a $\frac{1}{4}$ -inch mesh screen. The results shown apply only to rather large aggregates and may not relate closely to stable

TABLE 1

Comparative stability of 1-gm. surface soil and subsoil aggregates from the same soil profile, as measured by slaking after air-drying and by resistance to falling water drops*

SOIL TYPE	PROFILE NUMBER	SURFACE			SUBSOIL		
		Depth	Slaking	Number of Drops† to Destroy	Depth	Slaking	Number of Drops† to Destroy
		<i>inch</i>	<i>per cent</i>		<i>inch</i>	<i>per cent</i>	
Catalina clay	I	0-7	2	500+	8-100	80-100	0
	II	0-3	2	500+	36-42	100	0
Cialitos clay	I†	0-4	2-15	40-88	6-18	100	0
	II	0-13	—	500+	24+	90-100	1
Mucara silty clay loam	I	0-6	2	43	8-30	20-90	16-0
	II	0-3	—	500+	8-12	—	76
Aguirre clay	I	0-6	15	12	6-72	15-100	4
Nipe clay	I	0-8	0	500+	12+	25-75	100-80
Coamo clay	I	0-3	10	10	13-17	98	1
Santa Isabel clay	I	0-6	93-95	1 or less	6-72	97	1
Utuado sandy loam	I	0-3	1	variable 185-500	6-12	10-60	5
Matanzas clay	I	0-6	1	120	—	—	—
Bayamon sandy loam	I	0-4	1	36	4-60	5-100	10-0
Coto clay	I	0-4	1	500+	26-42	100	0
Ponceña clay	I	0-6	15	10	—	—	—
Amelia clay	I	0-3	2	115	9-18	55	6

* Each result represents values for 6 to 40 individual aggregates; averages are shown where replicate values were close to the averages; in other cases the extreme range is indicated.

† Number of drops times 5.6 equals ergs of energy per milligram soil, or 5,600 ergs per drop of water (8).

‡ The surface 3 feet of this profile was removed about 10 years ago.

TABLE 2

Comparative stability of 1-gm. surface soil and subsoil aggregates as measured by resistance to water-drop impact*

SOIL TYPE	SURFACE SOIL		SUBSOIL	
	Depth	Number of Drops† to Destroy	Depth	Number of Drops† to Destroy
	<i>inch</i>		<i>inch</i>	
Nipe clay.....	0-8	500+	12+	400
Cialitos clay.....	0-4	400	6-18	20
Mucara clay.....	0-6	400	20-30	3
Santa Isabel clay.....	0-4	10	20-26	1
Coto clay.....	0-6	500+	26-42	1

* The effect of air-slaking was eliminated by evacuating the dry aggregates and wetting in a partial vacuum with about 0.1 atmosphere of air pressure. Each result represents an average of five replicate aggregates.

† Number of drops times 5.6 equals ergs of energy per milligram of soil, or 5,600 ergs per drop of water.

microaggregates. With the 1-gm. aggregates, selected to represent the largest units generally desirable in surface soil under most field conditions (8), influences of organic matter are probably dominant. Other factors such as quantity and nature of clay and exchangeable cations may cause great differences in the microaggregation of various subsoils.

Nipe subsoil showed more stability than any other subsoil units tested, but 1-gm. surface soil aggregates, even of Nipe, were much more stable than were those from Nipe subsoil. This soil type, which is classed as a laterite, represents a rare, extreme case in Puerto Rico, being found only on serpentine rock, low in silica. The Mucara subsoil showing considerable stability (table 1) was probably partly weathered rock material rather than true clay aggregates. In shallow soils the distinction is not always clear between softened, altered rock and aggregated soil.

To eliminate air-slaking as a factor, samples have also been evacuated while dry, then wetted under the vacuum and tested with water drops (8). Table 2 shows some results of such testing, which indicate that large (1 gm.) subsoil and surface soil aggregates are quite different even when air-slaking is avoided.

SOME TYPICAL SOIL STRUCTURAL CONDITIONS

A number of soil profiles have been examined, described, and sampled in our studies throughout Puerto Rico. It is not feasible to present detailed descriptions of complete profiles here, but to point out some of the main structural types and conditions that are typical of Puerto Rican soils, the following generalized descriptions, based on the terminology outlined, seem justified:

Surface soil of slightly eroded Catalina-Cialitos clay from the western part of the island (mature, lateritic clay soil from tuffaceous rock). Strongly developed, subangular, $\frac{H}{V} = 1$, 10 mm., fine porosity, moderately stable, medium packing, normal cohesion.

Subsoil of Catalina-Cialitos clay from the western part of the island. Strongly developed, angular, $\frac{H}{V} = 1.2$ to 2.0, 10 mm., very fine porosity, unstable (exposed at the surface), 25 per cent overlap, $O > H > V$ cleavage, dense packing, strong cohesion.

Surface of moderately eroded Utuado sandy loam (young soil from quartz diorite rock). Moderately developed, rounded, $\frac{H}{V} = 1$, 6 mm., coarse porosity, moderately stable, loose packing.

Subsoil of deep phases of Utuado sandy loam. Weak, rounded, $\frac{H}{V} = 1$, 5 mm., coarse porosity, unstable, medium to dense packing, very weak cohesion.

Surface of Santa Isabel clay (immature soil, subhumid area, from mixed alluvium, above overflow). Moderately developed, rounded, $\frac{H}{V} = 1$, 2 mm., medium to fine porosity, moderately stable, loose packing, strong cohesion.

Upper subsoil of Santa Isabel clay. Moderate, subangular, $\frac{H}{V} = 2-4$, 2-4 mm. (vertical dimension), medium to fine porosity, unstable, 50 per cent overlap, $H = O$ cleavage, medium packing, strong cohesion.

Surface soil of Nipe clay (laterite from serpentine rock). Strongly developed, rounded, $\frac{H}{V} = 1$, 5 mm., medium to fine porosity (mostly fine), stable, loose packing, very weak cohesion.

Subsoil of Nipe clay. Strongly developed, subangular, $\frac{H}{V} = 1$, 5 mm., medium to fine porosity (mostly fine), moderately stable, 10 per cent overlap, loose packing, very weak cohesion.

Surface soil of Mucara silty clay loam (young or immature soil from hard pyroclastic rock). Moderately developed, rounded, $\frac{H}{V} = 1$, 8 mm., medium porosity, moderately stable, medium packing.

St. Lucie sand is an example of a nonaggregated soil with very weak cohesion. The most nearly nonaggregated, undisturbed soils with fine texture are silty clay subsoils from areas of high rainfall and black alkali from local arid areas.

The best developed angular structural units with long vertical axes ($\frac{H}{V} < \frac{1}{3}$) have been seen in certain strongly alkaline clay subsoils under semiarid climate in the Island of Vieques. Weakly formed subsoil units with $\frac{H}{V} < \frac{1}{2}$ have been seen in high terrace, lateritic soil profiles of Torres silty clay at several locations in Puerto Rico proper. This kind of structure is not common or prominent.

Very strongly developed, angular aggregates of 25 to 50 mm. diameter, with very fine internal porosity, $H = V$ cleavage, and $\frac{H}{V} = 1$, have been observed in old, strongly leached, high terrace soils with pale color and apparently slow internal drainage. Tendencies toward this condition are sometimes seen in Catalina and Cialitos clay.

GENERAL DISCUSSION AND CONCLUSIONS

Most of the soils of Puerto Rico contain relatively high clay contents, and the clay is usually found in well-defined aggregates. Essentially nonaggregated conditions are found only in certain special situations. These include some surface soils that are low in organic matter and some subsoils of the wet, or rain forest, upland part of the island, where average annual rainfall is 120 to 200 inches and the soil is continuously wet for long periods. Very limited areas of dark, alkaline soils of the semiarid area are also either very coarsely aggregated or essentially nonaggregated. In addition, clay upland soils that have been heavily trampled by people or animals or compacted by farm implements or machinery show little or no surface aggregation. The water intake capacity of all such nonaggregated clay surfaces is very low, and the runoff is correspondingly high. The trampled (mechanically packed) condition mentioned is most common around houses and barns and along paths, and it accounts for common observations of very high runoff from such locations.

Relations to texture

The observable internal porosity of soil aggregates is related, in a very general sense, to texture. The most common condition is for clay aggregates to have fine or very fine observable internal porosity. As mentioned by Baver (1), this is true to a considerable degree even with Nipe clay, often cited as a true laterite.

Coarser internal porosity of clay aggregates has been observed in some of the yellow and red, strongly lateritic, deep, clay soils derived from tertiary limestone, such as Matanzas, Coto, and Bayamon [see Roberts for descriptions (5)]. Coarse or medium internal porosity is observable only in certain aggregates of these soils. Other aggregates of the same soils have only very fine porosity. The contrast between the two different kinds of aggregates is very definite in some cases. The aggregates with very fine porosity are angular; those with medium or coarse porosity are rounded and small (<5 mm. diameter).

Soils with coarser texture, such as Utuado sandy loam or loam and Las Piedras loam (all from quartz diorites), are commonly aggregated into rounded units with medium or coarse internal porosity.

Relatively shallow upland soils of the interior hills and mountains at rainfall below 100 inches, with silty clay loam textures, normally have aggregates with medium or fine internal porosity, but the porosity is often noticeably coarser than for most soils with heavier clay textures.

Some of the densest surface soil aggregates observed have been in the chernozemlike clay soils, Coamo and Amelia. Virtually no internal porosity can be observed in their sharply angular aggregates. The clay contents of these soils are rather high.

Some aggregate size relationships

Surface soil aggregates of the normal, fertile soils of the subhumid south coastal plain are consistently smaller than surface soil clay aggregates of the humid, nonirrigated part of the island. The comparatively small aggregates of the south coastal area are normally coarse enough for rapid water intake during irrigation but are markedly erodible by channel flow of water.

Nipe clay soil (laterite), certain dark red phases of Catalina clay (near Comerio), and the rounded porous units noted in some of the lateritic soils over Tertiary limestone break readily into smaller aggregates than do most of the other clay soils of the humid area. Rapid water intake and transfer among the medium or small aggregates of Nipe (variable from about 0.5 mm. to 5 mm.) seem to be associated with relatively loose packing of the aggregates. The tendency toward fineness of aggregates as indicated seems to accompany the soil condition commonly called strong laterization. Weak cohesion within the soil is probably one reason for the small aggregates.

With subsoils in general it is believed that fine aggregates or microaggregates, are more stable against slaking and water-drop or washing action than are coarse aggregates. The situation is apparently quite different with surface soil, where, as shown in the tables, coarse aggregates are commonly stable.

Some aggregates originate with rock weathering

It is suggested that the subsoil structure of many residual soils in Puerto Rico can be said to originate with rock weathering. The units are preserved or modified by soil-forming processes. Exfoliation is commonly observed in the weathering of tuffaceous or andesitic rocks. The thin layers which break off by this process

are a natural basis for formation of typical, angular, medium or loosely packed subsoil aggregates. Near the rock the weathered layers are of variable orientation, but there is seldom any consistent tendency toward unequal axes in the actual soil aggregates derived from rock that weathers by exfoliation.

Some subsoil structures with dominant horizontal cleavage appear to originate by the weathering of strongly layered rocks, especially the tuffaceous shales. The rock cleavage appears to be carried over into the normally shallow soils from such rocks. A tendency toward long horizontal cleavage is evident in some Santa Isabel clay, an alluvial soil. This is believed to be inherited from sedimentary microbedding in the parent alluvium.

Rounded, porous subsoil aggregates appear to form consistently by weathering of grained quartz diorites and with certain coarse-textured pyroclastic rocks, in which weathering consists of some changes in the ground mass with a consequent loosening of the sand sized fragments or grains. The grains, except quartz, are commonly altered to clay minerals, but the original structure created by rock weathering appears to carry over into the subsoil.

Aggregate stability relationships

Subsoil macroaggregates may be quite distinct and essentially in equilibrium with their environment, but as indicated by the data, they are normally unstable when subjected to conditions such as drying and air-slaking, mechanical compaction, or water-drop impact. Surface soil macroaggregates, containing considerable organic matter, on the other hand, are much more resistant to these normal forces of destruction which act on exposed soil surfaces.

In discussing aggregate formation, Bradfield (2) said that "granules are probably formed more easily and once formed are more stable if they are formed from colloidal material which is in the flocculated state." Emphasis on the important roll of microaggregation by Baver (1) and on both floccstructure and microstructure by Schuylenborgh (6) agrees with Bradfield's view regarding flocculation. In Puerto Rico, flocculation is the common state of most soil colloids except in part of the arid south coastal area. But in many cases the flocs are too small to be seen with the naked eye. In these cases the aggregates appear to be nonporous. They apparently lack good "microstructure," as the term is used by Schuylenborgh. Many earthworm casts of clay surface soil are an excellent example of very stable units that have no visible porosity. Other stable surface soil units tend to show more visible porosity. Since earthworm casts, however, are commonly stable and also very dense, with no visible porosity, and certain other stable surface aggregates are very dense, it appears doubtful that very coarse flocs (microaggregates) and visible pores have any direct relation to the aggregate stability differences shown by the data in this paper.

Nipe clay subsoil aggregates (laterite) are more resistant to slaking and to raindrop impact than are most other subsoil aggregates, but Nipe surface soil aggregates containing organic matter (2 to 4 per cent in most cases) are much more stable than corresponding subsoil units.

Structure and permeability

We have not refined or tested our observations of field clues as a basis for permeability predictions to the same extent as has O'Neal (4), but certain broad relationships are evident. With aggregates that have coarse or medium-sized internal porosity patterns, measured percolation rates have all been greater than 1 and often above 10 inches per hour [with completely saturated soil cores under a hydraulic head equal to the length of the core (7)]. Catalina clay subsoil from the west end of the island has given percolation rates from about 0.5 to 2 inches per hour, with angular aggregates of very fine porosity. Santa Isabel and San Anton subsoil layers above the gravel commonly have percolation rates from 0.2 to 2 inches per hour. Rates below 0.02 inch per hour (very low permeability) have been obtained in some samples of Caguas clay, Mabi clay, Guayama clay, and Coloso clay subsoil. In all of these cases the aggregates are angular, have very fine (no visible) internal porosity, and seem to be densely packed. Some of the aggregates have been large (> 20 mm. diameter), and some have shown rather high percentages of overlap. Further details have not yet been worked out.

With Nipe subsoil (laterite), rapid percolation rates are apparently associated with loose packing of the subsoil aggregates. There is also little or no overlap of the predominantly small, subangular units.

Some lateritic subsoils, as already mentioned, appear to consist of two distinctly different kinds of structure: some of the aggregates are angular with no visible porosity, whereas others are small, rounded, and medium or coarsely porous. Observed percolation in the laboratory is mostly through the porous part of the soil, and rates have ranged from about 4 to 10 inches per hour (rapid rates).

SUMMARY

Accurate observations and descriptions of soil structure are indicated as needed for correlation with laboratory tests and with field performance. Some laboratory tests may lead to completely erroneous conclusions if interpreted without proper regard for desirable physical conditions that can be observed. To avoid terminology that may be misinterpreted, it is proposed to characterize soil structure as follows: 1. Distinctness; 2. Angularity; 3. Axial ratio; 4. Aggregate size; 5. Internal porosity; 6. Stability; 7. Aggregate overlap; 8. Direction of cleavages; 9. Closeness of packing (related to volume weight); 10. Cohesion among aggregates; 11. Moisture condition.

Laboratory results based on air-slaking and on water-drop impact, show that surface soil macroaggregates are much more stable than those from subsoils when both are subjected to conditions common at exposed surfaces. The differences are associated with the relatively high organic matter contents of surface soils. The stabilizing action is being studied in more detail. Water stability of macroaggregates is not consistently related to angularity or to visible internal porosity of the units.

Descriptions of typical structural conditions in selected soil types are offered; and certain relations to aggregate stability, permeability, soil use, texture, cli-

mate, and parent material are indicated. Rock weathering is suggested as one important process in the initial formation of structure in common soils from volcanic rocks. Internal porosity of aggregates corresponds to a certain degree with texture. Two distinctly different structural types occur in some strongly lateritic subsoils, and high percolation rates are apparently associated with the type of structure consisting of small, rounded, porous aggregates. Other relations of percolation to structure are suggested.

Future progress is expected in direct or indirect correlation of structural descriptions with water movement, aeration, and fertility, as well as with additional evaluations and explanations of aggregate stability.

REFERENCES

- (1) BAVER, L. D. 1950 Soil Physics, ed. 2. John Wiley & Sons, New York.
- (2) BRADFIELD, R. 1950 Soil Structure. *Trans. 4th Internatl. Cong. Soil Sci.* 2: 9-19.
- (3) NIKIFOROFF, C. C. 1941 Morphological classification of soil structure. *Soil Sci.* 52: 193-212 (as mimeographed, with modifications, and adopted by the inspectors of the Soil Survey Division of BPISAE, USDA, at Lincoln, Nebr., 1944).
- (4) O'NEAL, A. M. 1949 Soil characteristics significant in evaluating permeability. *Soil Sci.* 67: 403-409.
- (5) ROBERTS, R. C. 1942 Soil survey of Puerto Rico. Coop. Soil Survey Division, USDA, and Puerto Rico Agricultural Experiment Station. U. S. Dept. Agr. Bul. Ser. 1936, No. 8.
- (6) SCHUYLENBORGH, J. VAN 1947 A Study of Soil Structure. Firma Ponsen and Looyen, Wageningen.
- (7) SMITH, R. M., AND BROWNING, D. R. 1947 Some suggested laboratory standards of subsoil permeability. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 21-26.
- (8) SMITH, R. M., AND CERNUDA, C. F. 1951 Some applications of water drop stability testing to tropical soils of Puerto Rico. *Soil Sci.* 71: 337-345.

RECOVERY OF FERTILIZER NITROGEN BY OATS IN THE GREENHOUSE

W. V. BARTHOLOMEW AND A. E. HILTBOLD

Iowa Agricultural Experiment Station¹

Received for publication June 18, 1951

In field experiments using tracer techniques on ammonium nitrogen utilization by oats (1), it was observed that only a small part of the fertilizer applied to the soil could be recovered in the harvested crop. Moreover, the quantity of nitrogen normally contained in the recoverable part of the roots could account for only a small part of the unrecovered fertilizer. A large part of the fertilizer nitrogen remained in the soil in mineral form, had been lost in leaching or denitrification, or had been immobilized in the soil organic matter fraction. Since the oat crop did not appear to have had an abundance of nitrogen, it seemed unlikely that appreciable quantities of readily available nitrogen could have remained in the soil.

The experimental work herein reported was carried out in the greenhouse to measure residual mineral nitrogen in the soil after periods of cropping and fallow and to evaluate the magnitude of interchange between fertilizer and soil organic nitrogen. The recovery data in the crop and in the mineral forms in soil are reported here. The interchange calculations have been reported elsewhere (2).

MATERIALS AND METHODS

Greenhouse pot experiments of factorial design were set up to include the following treatments and conditions:

Main experiment

Soils	2	Marshall silt loam, Clarion silt loam
Organic additions	3	Alfalfa roots and crowns, cornstalks, check
Cropping systems	2	Oats, fallow
Rates of nitrogen application	1	80 lb. N per 2,000,000 lb. soil
Sampling dates	3	10, 37, 73 days after planting
Replications	3	

Supplementary experiment

Soils	2	Same as main experiment
Organic additions	2	Cornstalk, none
Cropping systems	1	Oats
Rate of nitrogen application	2	40 and 120 lb. per 2,000,000 lb. soil
Replications		

The Marshall soil was from Western Iowa and the Clarion from Central Iowa. They represent productive soils with medium high and medium low nitrogen contents. Only surface soils were used. Each soil was air-dried and thoroughly mixed,

¹ Journal paper J-1964 of the Iowa Agricultural Experiment Station, Ames, Project 1070. Appreciation is expressed to the Coke Oven Ammonia By-Products Corp. and the Spencer Chemical Co. for funds supplied in support of this investigation.

after which samples weighing 1,800 gm. were placed in $\frac{1}{2}$ -gallon glazed pots for the incubation and cropping experiments.

The organic amendments were chosen to represent wide and narrow C-N ratios. The corn contained 0.58 and the alfalfa residues 2.25 per cent nitrogen. The plant materials were washed free of dirt, oven-dried, and ground to pass a 10-mm. sieve. The organic residues, at the rate of 4.5 gm. per pot, were thoroughly mixed with the dry soil at the time of potting.

All soils received phosphorus and potassium in solution at rates equivalent to 40 lb. P_2O_5 and 27 lb. K_2O per acre. The fertilizer nitrogen, enriched with N15, was added in solution as ammonium sulfate at the time the soils were wetted and prepared for incubation or seeding. Over the incubation and growing period, the soils were allowed normal drying with frequent additions of water sufficient to bring the soils back to 60 per cent of their water-holding capacity. All pots were watertight to prevent loss of nitrogen in drainage.

At each sampling date, pots were selected at random from each experimental treatment. Tops and roots of the oat plants were harvested and prepared for determination of total nitrogen. The soil was air-dried and the entire 1,800 gm. extracted by mixing with two parts of $N NaCl$ acidified to pH 1. Large aliquots of the supernatant extract were analyzed for mineral nitrogen by distillation with Devarda's alloy. Total nitrogen was determined in the plant materials by a modified Kjeldahl procedure.

Determinations of N15 in excess of natural occurrence were made on the nitrogen samples recovered from both the soil and the plant materials.

The first sampling of the experimental treatments was made immediately after the nitrogen addition and wetting of the soils at the beginning of the experiment. This sampling provided a measure of efficiency in the recovery procedure and established a starting point from which subsequent changes in the nitrogen status of the soils could be measured. The soils in this initial sampling were spread out and air-dried immediately after fertilization and wetting, thus minimizing the possibility of microbial action on the added nitrogen. Mineral nitrogen was then extracted and determined by the procedure described.

RESULTS AND DISCUSSION

A three-letter system of coding is used to facilitate the tabular presentation of the data. The first letter represents the soil (M = Marshall and C = Clarion), the second letter the organic amendment (A = Alfalfa, C = cornstalks, and - = no addition), and the third letter the cropping system (F = fallow and O = oats).

The crop yields for the various treatments and the nitrogen content of the crops are shown in table 1. Total nitrogen uptake is shown in table 2, and percentage recovery of fertilizer nitrogen added to the soil, in table 3. Analyses of variance have been made of the yield, the nitrogen uptake, and the percentage recovery of added fertilizer by combining the data in two ways. In one set of analyses, comparisons were made on the two soils, two dates of sampling, three soil treatments, and three replications at one rate of nitrogen application, 80

TABLE 1
Yield and nitrogen content of oats at 37 and 73 days
Averages of three replications per pot

SOIL AND TREATMENT*	FERTILIZER ADDED PER POT	37-DAY SAMPLES		73-DAY SAMPLES	
		Yield per pot	Nitrogen	Yield per pot	Nitrogen
	<i>mgm.</i>	<i>gm.</i>	<i>per cent</i>	<i>gm.</i>	<i>per cent</i>
MAO	73	6.98	1.23	8.62	0.98
MCO	36.5			4.32	0.91
	73	6.06	0.89	7.10	0.85
	109.5			9.25	0.95
M-O	36.5			7.60	0.83
	73	7.39	1.35	8.95	0.97
	109.5			10.89	1.09
CAO	73	8.35	1.11	7.70	1.06
CCO	36.5			4.45	0.88
	73	7.37	0.77	6.17	0.84
	109.5			7.42	0.97
C-O	36.5			6.50	0.84
	73	6.20	1.36	7.60	1.15
	109.5			8.35	1.20

* See text for explanation.

TABLE 2
Plant nitrogen uptake by oats at 37 and 73 days
Averages of three replications, in milligrams per pot

SOIL AND TREATMENT	FERTILIZER N ADDED	37 DAYS			73 DAYS		
		Plant N total	Source of N		Plant N total	Source of N	
			Fertilizer	Non- fertilizer		Fertilizer	Non- fertilizer
MAO	73	85.6	32.8	52.8	84.2	29.1	55.1
MCO	36.5				39.2	10.0	29.2
	73	53.6	29.6	24.0	60.2	29.6	30.6
	109.5				87.9	52.7	35.2
M-O	36.5				63.3	13.5	49.8
	73	99.0	42.9	56.1	86.7	34.6	52.1
	109.5				119.0	58.9	60.1
CAO	73	92.7	34.1	58.6	81.5	28.5	53.0
CCO	36.5				39.0	11.5	27.5
	73	55.4	31.2	24.2	51.8	24.5	27.3
	109.5				71.8	39.3	32.5
C-O	36.5				54.8	14.4	40.4
	73	84.1	41.0	43.1	87.4	39.2	48.2
	109.5				99.9	51.8	48.2

* See text for explanation.

lb. N per acre. In a second set of analyses, comparisons were made of the two soils, two soil treatments, three rates of nitrogen application, and three replications but at only one date of sampling, 73 days after planting. The summary of mean squares is shown in table 4.

There were no significant differences in yield or total nitrogen uptake between the two soils at the 37th day when the oats were in the boot stage. At 73 days, however, when the oats were mature, yields and total nitrogen uptake from the Marshall soil were significantly higher than those from the Clarion soil. The average yield of oats increased significantly during the 37- to 73-day period, the larger gains occurring on the Marshall soil. Total nitrogen uptake, however, was

TABLE 3
Recovery of fertilizer nitrogen in oat crop

SOIL AND TREATMENT*	FERTILIZER N ADDED PER POT	ADDED NITROGEN RECOVERED IN OAT CROP	
		37 days	73 days
	<i>mgm.</i>	<i>%</i>	<i>%</i>
MAO	73	44	40
MCO	36.5		27
	73	41	41
	109.5		48
M-O	36.5		37
	73	59	47
	109.5		54
CAO	73	47	39
CCO	36.5		32
	73	43	34
	109.5		36
C-O	36.5		39
	73	56	54
	109.5		47

* See text for explanation.

not significantly higher at 73 days than it was at the earlier date. Both the yield of oats and their uptake of nitrogen were markedly reduced by the addition of corn residues to the soil. There were, however, no differences in either yield or nitrogen uptake between soils receiving alfalfa residues and soils to which no organic addition was made. There was approximately a linear response in both yield and nitrogen uptake to increasing rates of fertilizer application.

The amount of fertilizer nitrogen present in the oat crop was higher at 37 days than at 73 days. The average recovery of fertilizer nitrogen at the time the oats were in the boot stage was 48 per cent of that applied, whereas at maturity the crop contained only 42 per cent of the applied nitrogen. The loss of fertilizer nitrogen from the crop was generally accompanied by gains in nitrogen derived from nonfertilizer sources. From the boot stage to maturity, therefore, the crop had been actively absorbing nitrogen from and losing nitrogen to the soil, the total nitrogen in the crop remaining about constant. The loss of nitrogen could

perhaps be accounted for in the death and loss of leaves and roots as the plants approached the harvest stage.

The influence of plant residues in reducing recovery of fertilizer nitrogen was marked. Approximately 50 per cent of the applied fertilizer nitrogen was recovered at the harvest stage in oats grown where no crop residues had been added to the soil, whereas 38 per cent recovery was the average for crops from corn- or

TABLE 4

Summary of mean squares from the analysis of variance of crop yields, nitrogen uptake, and percentage fertilizer recovery

SOURCE OF VARIATION	df	YIELD MEAN SQUARE	NITROGEN UPTAKE (TOTAL) MEAN SQUARE	PERCENTAGE RECOVERY OF FERTILIZER MEAN SQUARE
Soils (Marshall, Clarion)	1	0.73	64.00	0.03
Dates (37, 73 days)	1	3.55**	87.11	318.03**
Treatments (alfalfa, corn, none)	2	4.66**	4,242.70**	706.70**
Soils \times dates	1	5.36**	4.00	3.36
Soils \times treatments	2	2.25*	68.25	14.53
Dates \times treatments	2	1.76	50.36	6.03
Soils \times dates \times treatments	2	1.07	162.59*	62.53*
2(CO) \times (AO + -O)	1	8.47**	8,425.35**	
(AO) \times (-O)	1	0.85	57.04	
2(-O) \times (CO + AO)	1			1,343.35**
(CO) \times (AO)	1			70.04*
Error	24	0.44	26.04	12.81
Soils (Marshall, Clarion)	1	14.56**	641.78**	34.02
Treatments (corn, none)	1	30.43**	6,507.11**	950.69**
Rates R(40, 80, 120 lb N/acre)	2	31.89**	6,257.03**	510.25**
Soils \times treatments	1	0.75*	1.78	66.70*
Soils \times rates	2	4.52**	184.70*	116.87*
Treatments \times rates	2	1.57**	103.36	21.03
Soils \times treatments \times rates	2	0.11	56.70	44.19
R ₁ \times R ₂ + R ₃	1	49.67**	9,270.68**	990.12**
R ₂ \times R ₃	1	14.10**	3,243.38**	30.38
Error	24	0.21	33.50	16.11

* Significant at 5 per cent level.

** Significant at 1 per cent level.

alfalfa-treated soils. Corn residues reduced recovery more than did alfalfa. Both the difference between residues and no residues and the difference between corn and alfalfa are statistically significant.

An interesting observation on the recovery at varying rates of application is that a significantly smaller proportion of the 36.5-gm. per pot or 40-pound per acre rate of application was recovered in the crop than of the higher rates, 80 or 120 lb. per acre. Moreover, the recovery at the 120-lb. rate was greater than that at the 80-lb. rate, although the difference was a little short of that required for significance at the 5 per cent level of probability. These trends of greater recov-

ery at the higher rates suggest that in some way a larger proportion of the lower rate of application was made unavailable to the crop.

Mineral nitrogen recoveries by soil extraction are shown in table 5 for both the cropped and the fallow soils. Recoveries at the beginning were determined on only one set of samples. The means of the results were used as the initial nitrogen content. Since plant growth at the end of 10 days was negligible, the

TABLE 5
Recovery of nitrogen in soil extracts
Averages of three replications, in milligrams per pot

SOIL AND TREATMENT*	FERTILIZER ADDED	MINERAL-N EXTRACTED FROM SOIL								
		0 days		10 days		37 days		73 days		
		Fertilizer	Non-fertilizer	Fertilizer	Non-fertilizer	Fertilizer	Non-fertilizer	Fertilizer	Non-fertilizer	
Cropped soils										
MAO	73.0	49.2	55.0	45.5	61.1	1.1	18.6	0.9	25.7	
	MCO	36.5	20.6	50.2				0.4	26.8	
		73.0	53.4	40.2	40.6	45.4	1.3	19.9	1.0	24.8
		109.5	73.6	50.0					0.7	24.7
M-O	36.5	21.6	47.8					0.4	23.1	
		73.0	53.1	37.4	51.5	62.8	1.2	20.7	0.9	24.4
		109.5	68.9	55.7					0.5	18.9
	CAO	73.0	51.1	52.0	44.9	61.2	1.0	21.4	1.3	26.4
CCO	36.5	22.3	34.8					0.3	21.6	
		73.0	53.0	40.6	41.7	46.3	0.9	23.3	0.8	23.5
		109.5	67.7	44.3					0.9	20.8
	C-O	36.5	21.1	35.6					0.4	20.8
	73.0	53.0	39.9	50.3	60.6	1.1	19.2	0.8	22.7	
	109.5	75.1	39.0					0.6	20.7	
Fallow soils										
MAF	73.0	49.2	55.0	43.7	61.7	42.0	86.8	32.9	107.1	
MCF	73.0	53.4	40.2	38.5	40.8	34.6	51.6	17.7	70.7	
M-F	73.0	53.1	37.4	49.7	66.6	47.2	73.2	36.1	91.4	
CAF	73.0	51.1	52.0	40.4	58.6	41.3	81.8	30.0	91.5	
CCF	73.0	53.0	40.6	44.1	49.0	29.6	42.8	20.3	53.4	
C-F	73.0	53.0	39.9	49.9	49.4	42.7	66.5	35.4	77.1	

* See text for explanation.

cropped series in this sample was a replicate of the fallow. By the time the oats were in the boot stage, at 37 days, very little nitrogen remained in inorganic form in the cropped soils. The residual fertilizer constituent of the soil mineral nitrogen had almost disappeared and the nonfertilizer mineral nitrogen was low. At this stage, there were no differences in content of mineral nitrogen between soils, treatments, or nitrogen additions. At 73 days, the mineral fertilizer component in the cropped soils had been further reduced, but in general the non-

fertilizer fraction had been increased beyond the amount present at the previous sampling.

In the fallow soils, the mineral fertilizer component continued to decrease gradually throughout the incubation period. It decreased more rapidly where organic materials had been applied. Corn fodder had a more pronounced influence than did alfalfa. With the exception of the corn-treated soils, the amount of nonfertilizer mineral nitrogen in fallow soils continued to increase during the experimental period. Where corn residues had been added, there was an initial decline in nonfertilizer mineral nitrogen, which was followed by a gradual increase toward the end of the experimental period. The total mineral nitrogen contents of corn-treated fallow soils remained lower at the conclusion of the period than they were at the beginning.

These results serve to demonstrate the interchange of nitrogen between organic and mineral forms in the soil. Since the fertilizer constituent was labeled, it was possible to measure directly its removal from the soil mineral nitrogen supply as it was utilized by the crop and various transformations in the soil. The nonfertilizer constituent, however, was not labeled, and although it proceeded through the same transformations as did the fertilizer constituent, its rate of removal from the mineral nitrogen supply could not be measured directly by the net difference in amounts present initially and at the end of the period. The reason for this is that while nonfertilizer mineral nitrogen was being utilized along with fertilizer nitrogen in proportion to its concentration in the soil mineral nitrogen supply, it was being continuously supplemented by mineral nitrogen released from organic sources in the soil. In the untreated fallow soils, mineralization more than compensated for the immobilization of nitrogen, although both processes were occurring simultaneously. This is indicated by the continual decline of the fertilizer constituent at the time when the total mineral nitrogen supply was increasing.

At the beginning of the experiment, fertilizer nitrogen could not be quantitatively recovered with N NaCl solution acidified to pH 1. This initial fixation against extraction ranged from about 15 mgm. per pot at the lower rate of nitrogen application to about 21 and 38 mgm., respectively, at the successively higher rates.

Fixation of ammonia against various extracting solutions has been demonstrated by a number of investigators. McBeth (3), in studying the nitrifying power of semiarid soils at different depths, observed that large quantities of ammonia were fixed against extraction either with 10 per cent HCl or boiling 10 N KOH or NaOH. Fixation was higher from concentrated than from dilute solutions and greater at high than at low temperatures. Total ammonia fixation against leaching by 10 per cent HCl ranged from about 2.8 me. per 100 gm. in a subsoil from Lordsburg, California, to less than 0.13 me. per 100 gm. in a topsoil from Berwyn, Maryland, when a total of 3.57 me. per 100 gm. was added to the soil in solution.

Olsen (5) observed that ammonia was strongly adsorbed on soil colloids but concluded that quantitative recovery could be obtained by leaching with a

N KCl solution containing sufficient HCl to lower the pH to 1. Stanford² concluded that N acetic acid would remove more ammonia from soil than would neutral N KCl but that the fixed ammonia was not extracted by either treatment. Stanford's conclusion is confirmed by the data in table 5.

The fertilizer composition of the crop nitrogen (table 2) bears little relationship to the fertilizer composition of the nitrogen extracted from the soil by an acid solution of NaCl (table 5). The soil extracts contained considerable non-fertilizer nitrogen in excess of that available to the plant.

The fate of the fixed ammonia remains unknown. Fixed potassium is slowly released when the concentration of the exchangeable form becomes low. It seems likely that ammonia would react similarly.

Total percentage recoveries of the fertilizer nitrogen in the plant and from the soil extracts are shown in table 6. In general, in the pots receiving alfalfa

TABLE 6
Total recovery of fertilizer nitrogen in the crop and from the soil extract
Average of three replications

SOIL AND TREATMENT*	RECOVERY OF FERTILIZER NITROGEN			
	37 days		73 days	
	Fallow	Cropped	Fallow	Cropped
	%	%	%	%
MAO	57.5	45.5	45.1	41.2
MCO	47.4	42.8	24.2	42.4
M-O	64.7	60.6	49.5	48.2
CAO	56.6	48.4	41.1	40.8
CCO	40.5	44.2	27.8	35.1
C-O	58.5	57.5	48.5	55.1

* See text for explanation.

residues and in the unamended pots, a greater proportion of the nitrogen fertilizer was recovered from the fallow than from the cropped soils. In the pots receiving cornstalk residues, considerably less nitrogen was recovered at the 73-day sampling in the fallow than in the cropped soils.

Recovery in the oat crop of ammonium nitrogen applied as fertilizer has been consistently low. Seldom, even in what has been considered the most favorable environments, has recovery been greater than 50 per cent of that applied. Norman *et al.* (4), studying fixation of nitrogen by soybeans, recovered 53 to 69 per cent of the nitrogen applied as ammonium nitrate when the ammonium ion only was labeled. In a similar study, but employing labeled nitrogen as $\text{Ca}(\text{NO}_3)_2$, 74 to 100 per cent of the added nitrogen was recovered in the crop. Thornton (6), likewise using tagged nitrate, recovered 71 to 98 per cent of the applied nitrogen.

² Stanford, G. Potassium fixation in soils as affected by type of clay mineral, moisture conditions, and concentration of other ions. 1947. [Unpublished doctor's thesis. Copy on file Iowa State College Library, Ames.]

Since leaching losses were prevented and significant denitrification losses were improbable, the conclusion seems justified from the current study that more than half of the ammonium nitrogen applied was either fixed by the soil in unavailable form or immobilized into soil organic matter. An analysis of the nitrogen interchange data (2) indicates that immobilization into soil organic matter can account for the larger part of the unrecovered nitrogen but that fixation must also be considered as an important phenomenon in the use of ammonium nitrogen as a fertilizer.

SUMMARY AND CONCLUSIONS

Isotopic nitrogen N¹⁵ was used in greenhouse pot experiments with oats to measure recovery of fertilizer nitrogen as affected by rate of application and treatment of the soil with crop residues.

Plant yield and nitrogen uptake were lower in soils to which corn fodder had been added than in soils to which alfalfa or no plant residue had been applied.

Fertilizer nitrogen in the cropped soils had essentially disappeared from mineral form, and plant uptake of the fertilizer constituent had almost ceased by the time the oats had reached the boot stage.

Plant uptake of nitrogen from the fertilizer increased in direct proportion to the rate of application. Recoveries in the total crop ranged from 27 to 54 per cent of the nitrogen applied. The lower percentage recoveries were generally associated with the lower rates of nitrogen application and with the addition of plant residues, especially corn, to the soil.

Changes in the mineral nitrogen contents of the cropped soils were compared to those of duplicate soils kept fallow during the growing period. In absence of crop withdrawal, residual fertilizer nitrogen decreased slowly and at the same time was diluted with nitrogen mineralized from organic sources. Under fallow conditions the supply of mineral nitrogen was larger at the end of the experiment than initially, except where corn residues had been added. Under cropping, mineral nitrogen contents decreased rapidly during the vigorous growth stage, irrespective of soil, treatment, or rate of nitrogen addition. The content of soil mineral nitrogen increased gradually as the crop matured.

REFERENCES

- (1) BARTHOLOMEW, W. V., NELSON, L. B., AND WERKMAN, C. H. 1950 Use of the nitrogen isotope N¹⁵ in field studies with oats. *Agron. Jour.* 42: 100-103.
- (2) HILTBOLD, A. E., AND BARTHOLOMEW, W. V. 1951 Use of tracer techniques in the simultaneous measurement of mineralization and immobilization of nitrogen in soil. *Soil Sci. Soc. Amer. Proc.* (1950) 15: 166-173.
- (3) McBETH, I. G. 1917 Fixation of ammonia in soils. *Jour. Agr. Res.* 9: 141-155.
- (4) NORMAN, A. G., AND KRAMPITZ, L. O. 1946 Nitrogen nutrition of soybeans: II. *Soil Sci. Soc. Amer. Proc.* (1945) 10: 191-196.
- (5) OLSEN, C. 1929 Analytical determination of ammonia in soil, and the adsorption power of soil for ammonia. *Compt.-Rend. Lab. Carlsberg* 17(15): 1-18.
- (6) THORTON, G. D. 1947 Greenhouse studies of nitrogen fertilization of soybeans and lespedeza using isotopic nitrogen. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 249-251.

EFFECT OF TILLAGE DEPTH ON SOIL CONDITIONS AND COTTON PLANT GROWTH FOR TWO ALABAMA SOILS

V. C. JAMISON, I. F. REED, C. M. STOKES, AND TOM E. CORLEY

U. S. Department of Agriculture and the Alabama Agricultural Experiment Station¹

Received for publication August 20, 1951

The effect of tillage in loosening soil is generally considered desirable in that physical conditions suitable for plant germination, emergence, and early growth are produced. Tillage methods used vary considerably as to depth, degree of inversion of the soil, and fineness of pulverization achieved. Various methods may be used on similar soils for growth of the same crop plant. Destruction of plow pans and occasional loosening of subsoil have proved beneficial to crops in the older agricultural areas of the United States (3, 12, 15, 18, 21) and elsewhere (22, 23, 24). On the other hand, no benefit and in some cases decreases in yield have resulted from deep tillage in the Middle West (17, 19, 26), the Great Plains (6, 25), and the intermountain West (4). Benefits were realized from deep tillage in one Missouri soil only when subsoil liming accompanied the tillage operation (28). Plowing to a medium depth of 6 to 8 inches is usually preferred to shallow or subsurface tillage (2, 9, 14, 20) for most crops, one exception being subsurface tillage of soils subject to serious erosion (1, 7). Some workers feel that the chief functions of plowing are to bury trash and help control weeds and insects. Other reports indicate that plants may be harmed by soil compaction (13, 21, 27).

Increased power requirements of deep tillage over ordinary methods make the study of the effects of tillage depth on soil properties and the growth of crops on various soils economically important. This progress report of the effects of tillage depth on growth of cotton plants in two Alabama soils is presented as additional information on tillage problems. It is believed that the differences in soil and plant reaction to tillage depth on the two soils may help explain the apparent discrepancies in deep tillage effects reported elsewhere.

EXPERIMENTAL METHODS

Two sets of experimental plots in Alabama were used for this study. One is near Prattville on Greenville fine sandy loam and the other near Belle Mina on Decatur clay. The Greenville soil has a fine sandy loam surface layer about 5 inches deep underlain with red, compact sandy clay. The Decatur soil possesses better than average internal drainage for a clay and is considered one of the more productive soils of the Southeast.

Nine tillage treatments replicated four times were laid out in a balanced lattice design (29) in 1948 on the Greenville soil. Subsequently two extra treatments were added outside the regular experiment, and the growth of a winter legume

¹ The first two authors (V. C. J. and I. F. R.) are with the Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture; and the last two (C. M. S. and T. E. C.), with the Alabama Agricultural Experiment Station, Auburn.

(vetch) as a variable was introduced in the winter of 1949-50. Treatments for the 1950 season were as follows: 1. Subsweeps; 2. Disk plow, no vetch; 3. Subsoil 18 inches, disk plow; 4. TNT plow; 5. Disk plow; 6. Graham-Hoerne tiller; 7. Moldboard plow; 8. Disk harrow; 9. Rotary tiller; and extras 11. Disk tiller and 12. Subsoil 18 inches, disk harrow.

All treatments were spring operations except the subsoiling, which was changed from spring to fall for the 1950 season. This operation was performed with a Windy subsoiler in the fall of 1949 during a period of dry weather when the shattering effect would be at a maximum. The plots were each 100 by 21 feet—six cotton rows wide. The soil was tilled with the chisel at 21-inch intervals, approximately in the rows and between the rows. The plots were planted March 31 with Smith 78 variety cotton seed and fertilized at the rate of 750 pounds per acre with a 4-10-7 mixture placed about 2 inches below the soil surface and $1\frac{1}{2}$ inches to the side of the seed.

Sixteen treatments replicated five times in a balanced lattice design were used on the Decatur soil. No winter cover crop was grown on this soil. The treatments were as follows for the 1950 season: 1. Rotary tiller, fall; 2. TNT plow, fall; 3. subsweeps, spring; 4. Disk harrow, spring; 5. Moldboard plow, fall; 6. Disk plow, fall; 7. Rotary tiller, spring; 8. Till-Mor, spring; 9. Moldboard plow, spring; 10. TNT plow, spring; 11. Subsoil 18 inch, disk plow, fall; 12. Till-Mor, fall; 13. Subsoil 12 inch, disk plow, spring; 14. Heavy disking, spring; 15. Disk plow, spring; 16. Subsoil 18 inch, disk plow, spring.

The plots were each 173 by 21 feet—six rows wide. The area was planted April 12, 1950 with Empire variety cotton seed and fertilized with 500 pounds of a 6-8-4 mixture per acre placed as in the Greenville soil.

Soil core samples were taken with a hammer sampler (10) at about the time the cotton was half grown (June 13 for the Greenville and July 5 for the Decatur soil in 1950). A record of the number of hammer blows required to cut each sample was taken as a measure of soil hardness.² The cores were weighed in the field condition, soaked on the tension table for 1 day, subjected to a tension of 60 cm water for 1 day, weighed, oven-dried, and weighed again. The field moisture percentage, total porosity, and "air space" or macroporosity were calculated for each core from the three weighings, core volume, and particle density of the soil. The particle density was based on 20 or more wet pycnometer determinations for each horizon sampled in the two soils. Soil weediness at harvest time was estimated in terms of the average number of weeds per square yard in each plot.

The average height of 20 randomly chosen plants in each plot at harvest time was taken as a measure of "mature plant height." The "relative rooting depth" was the average of 10 to 20 randomly measured plants in each plot, each measurement being the depth below the soil surface where the root diameter decreased to half the surface diameter. This measurement was initiated in the fall of 1950. All soil and plant measurements, including yields, were made on the center two rows.

² It has been shown (11) that for hardness measured in this way, macroporosity is closely related to $\log (W\sqrt{H})$ where W is the moisture percentage and H the number of hammer blows required to cut the core. Thus $\log (W\sqrt{H})$ or $f(W, H)$ is an approximate measure of soil porosity conditions.

RESULTS

There was little difference in yields due to treatment in 1948 on the Greenville soil. The cotton plants on the more deeply tilled plots were taller than those on the other plots, but late boll weevil infestation prevented maturity of many of the bolls on the late maturing plants, and therefore the yields for all treatments were about the same. Much better weevil control was achieved in 1949 and 1950. The TNT-plowed plots were superior to all others in 1949. In 1950, the fall-subsoiled plots yielded about the same as the TNT-plowed. The difference between either of these and the lowest yielding treatment (disk plow, no vetch) was highly significant. Where tillage was the only variable, the differences were significant only in the comparison of either of the deep tillage treatments with the subsweep treatment. Since the extra treatments were outside the balanced lattice, the results from these plots could not be included in the analysis. The mean yield of the subsoil, disk harrow (extra) treatment compared favorably with that of the subsoil, disk plow. Also, the disk tiller (extra) treatment mean yield was about the same as that of the disk harrow.

The results for 1950 on the Decatur soil showed no significant differences between individual tillage treatments.

Since the results on the Greenville soil were inconclusive and those on the Decatur soil appeared to show no differences due to different tillage methods, it was decided to group the treatments and analyze for the significance of group differences in the means of soil and plant measurements. The treatments were grouped as follows:

SHALLOW	MEDIUM	DEEP
<i>Greenville fine sandy loam</i>		
Subsweeps	Disk plow	Subsoil 18 inches, disk plow
Disk harrow	Moldboard plow	Subsoil 18 inches, disk harrow
Disk tiller	Graham-Hoeme tiller	TNT plow
Rotary tiller		
<i>Decatur clay</i>		
Subsweeps, spring	Disk plow, spring	Subsoil 18 inches, disk plow, spring
Disk harrow, spring	Disk plow, fall	Subsoil 18 inches, disk plow, fall
Heavy disking, spring	Moldboard plow, spring	Subsoil 12 inches, disk plow, spring
Rotary tiller, spring	Moldboard plow, fall	TNT plow, spring
Rotary tiller, fall	Till-Mor, spring	TNT plow, fall
	Till-Mor, fall	

The "no vetch" treatment was excluded to avoid a variable other than tillage. The shallow group comprises those tilled less than 5 inches deep; the medium group, between 5 and 7 inches; and the deep group, more than 7 inches. The effect of time of tillage was tested by combining the "fall" treatments in comparison with the same operations performed in spring on the Decatur soil. These two groups were analyzed for the significance of differences in plant measurements.

The effects of tillage depth on some soil characteristics are shown in table 1. The values for the function $f(W, H)$, approximate measurements of soil porosity conditions (11), are presented as supplements to the macroporosity values. The relatively high macroporosity values indicate that both these soils should be

permeable to water and air. Since soil cores were not taken in the shallow tillage treatments in the Greenville soil, porosity comparisons are limited to the deep and medium tillage groups for this soil. The mean difference between these groups in the 3-5½-inch depth was not significant, but in the 5-7½-inch depth the soil was more porous at sampling time in the deep tillage group. In the Decatur soil, the difference in porosity conditions between the shallow- and medium-tilled groups in the 3-5½-inch depth is significant. Although the macroporosity does not appear to be significantly greater for deep tillage than for either of the other groups in the 5-7½-inch layer, the hardness measurements indicate that this zone

TABLE 1
Comparison of soil characteristics as affected by tillage depth on two Alabama soils

TILLAGE TREATMENT GROUPING	MACROPORSITY		$f(H,W)^*$		WEEDINESS, PLANTS PER SQ. YD.
	3-5½-inch Depth	5-7½-inch Depth	3-5½-inch Depth	5-7½-inch Depth	
	%	%			
Greenville fine sandy loam					
Shallow.....	—	—	—	—	40.00
Medium.....	26.3	17.9	1.438	1.690	23.10
Deep.....	30.0	24.9	1.428	1.482	16.25
Least Significant Difference:					
5% Probability.....	11.4	3.56	0.119	0.123	7.41
1% Probability.....	—	—	—	0.182	9.95
Decatur clay					
Shallow.....	15.5	15.0	1.920	2.025	12.60
Medium.....	24.0	16.0	1.775	1.980	7.84
Deep.....	19.6	18.2	1.773	1.865	7.80
Least Significant Difference:					
5% Probability.....	7.97	3.74	0.155	0.102	4.74
1% Probability.....	—	—	—	0.151	6.28

* The base 10 logarithm of the product of the square root of the number of hammer blows required to cut a 470-cc. soil core times the moisture percentage. Thus $f(H, W) = \log (W\sqrt{H})$ where W is the soil moisture percentage and H the number of blows.

is significantly looser and more porous in the deep-tilled plots. The shallow-tilled plots on both soils were significantly weedier at harvest time than the other plots. Control of many kinds of weeds by inversion of soil and deep burial of the seeds has been reported by Chepil (5) and others.

The effects of tillage depth on cotton plant measurements are shown in table 2. The growth of cotton was different on the two soils. The relative rooting depth was greater but the plant heights and yields were less for the Decatur than the Greenville soil. The relationship of relative rooting depth to tillage depth was more significant than was that of yields or plant heights to tillage depth at either location. The difference in relative rooting depth was highly significant between deep and medium tillage groups and also between deep and shallow groups for

the Greenville soil, as well as between the deep and shallow groups for the Decatur soil. The yield difference was highly significant between the deep and the

TABLE 2

Comparison of cotton plant characteristics as affected by tillage depth on two Alabama soils

TILLAGE TREATMENT GROUPING	RELATIVE ROOT- ING DEPTH	MATURE PLANT HEIGHT	YIELD SEED COT- TON PER ACRE
Greenville fine sandy loam			
	<i>in.</i>	<i>in.</i>	<i>lb.</i>
Shallow.....	4.09	39.7	1661
Medium.....	4.49	39.9	1682
Deep.....	5.16	40.6	1943
Least Significant Difference:			
5% Probability.....	0.44	2.35	53
1% Probability.....	0.59	—	71
Decatur clay			
Shallow.....	5.87	33.7	1566
Medium.....	6.06	33.6	1557
Deep.....	6.42	35.3	1521
Least Significant Difference:			
5% Probability.....	0.34	2.8	109
1% Probability.....	0.45	—	—

TABLE 3

Comparison of cotton plant characteristics as affected by time of tillage on Decatur clay

TILLAGE TREATMENT GROUPING	RELATIVE ROOT- ING DEPTH	MATURE PLANT HEIGHT	YIELDS SEED COT- TON PER ACRE
	<i>cm.</i>	<i>in.</i>	<i>lb.</i>
Spring tillage.....	16.10	34.59	1568
Fall tillage.....	15.21	33.45	1522
Least Significant Difference:			
5% Probability.....	0.832	2.58	101
1% Probability.....	1.105	—	—

TABLE 4

Correlation coefficients between cotton plant characteristics on two Alabama soils

COMPARISONS	GREENVILLE FINE SANDY LOAM	DECATUR CLAY
Yield vs. mature plant height.....	+.576**	+.657**
Yield vs. relative rooting depth.....	+.488**	+.069
Mature plant height vs. relative rooting depth.....	+.210	+.181

** Significant at 1% probability.

medium or the shallow groups on the Greenville but not on the Decatur soil. Tillage depth appeared to have little direct effect on plant heights for either soil.

The effects of spring and fall tillage on cotton plant measurements for the Decatur soil are compared in table 3. The significant decrease in relative rooting depth with accompanying decreases in height and yield for fall tillage over spring indicates that fall tillage is probably inferior for this soil when cotton is grown year after year.

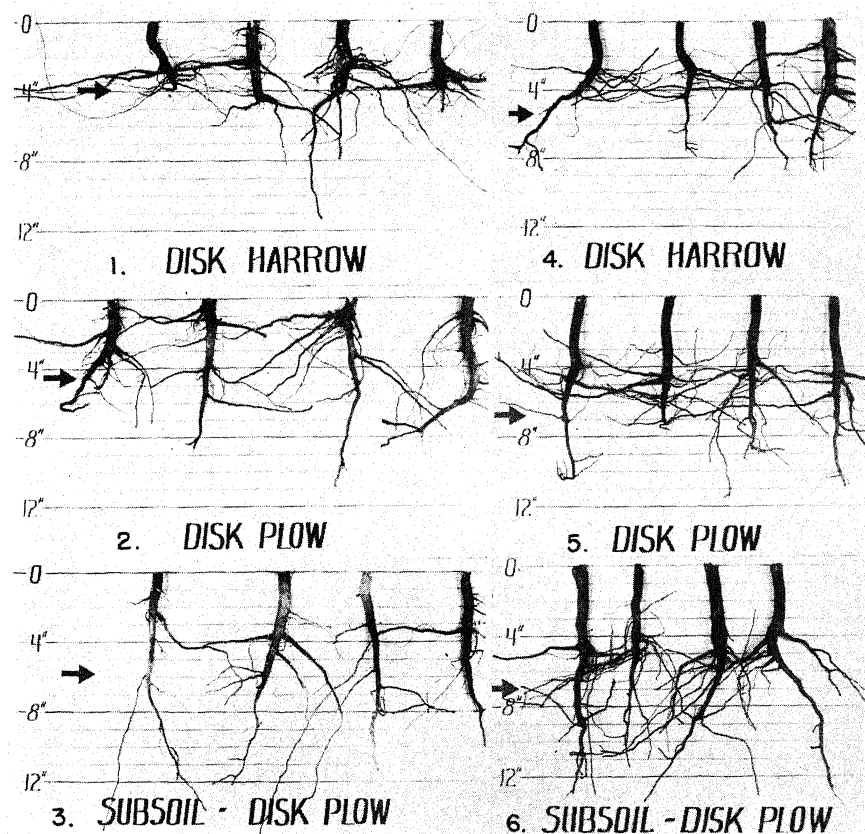


FIG. 1. EFFECT OF TILLAGE DEPTH ON CHARACTER AND RELATIVE ROOTING DEPTH OF COTTON

1, 2, and 3, roots from Greenville fine sandy loam; 4, 5, and 6, from Decatur clay. The arrow indicates the mean relative rooting depth for the treatment and soil.

The correlation coefficients between cotton plant measurements are shown in table 4. It has already been shown that tillage depth is related to cotton rooting depth in both soils and to yields from the Greenville soil. Since correlations between relative rooting depth and yield and also between yield and plant height are highly significant for the Decatur soil, deep tillage must have some indirect though not very pronounced effect on cotton plant height for this soil. With good weevil control, yields and stalk heights on the Decatur soil are closely correlated. Relative rooting depth was affected by tillage depth on the Decatur soil, but

since the correlations between relative rooting depth and yields or plant heights are not significant, tillage depth appears to have little effect on heights or yields on this soil.

DISCUSSION

The difference in the effects of deep tillage upon the growth of cotton on the two soils appears to lie in differences in soil properties in the zone below the normal plow layer. The Greenville subsoil, undisturbed by ordinary tillage methods, appears to impede the growth and penetration of cotton roots, limiting their extension to the shallow, sandy surface layer (fig. 1). The natural resistance of the compact subsoil may have been increased by a plow pan formed by years of plowing to a depth of about 5 inches, thus loosening the sandy surface but compressing the soil immediately beneath the plow layer. Penetrometer probings made in the summer of 1949 definitely indicated the presence of such a hard pan. Porosity, air composition, and fertility studies of the subsoil in these plots indicate that the limitation to rooting depth is not due to poor aeration or low nutrient content of the subsoil as reported elsewhere (13, 14, 16, 29). Poor root penetration in the shallow- and medium-tilled plots appears to be due to physical impedance as demonstrated by Veihmeyer and Hendrickson (27). The relatively deeper rooting of cotton in the Decatur soil than in the Greenville (fig. 1) must be due to some difference in subsoil properties other than macroporosity and hardness as measured by resistance to sampler penetration. The macroporosity values were lower and the hardness values were higher in the medium-tilled Decatur soil than those of the same tillage group in the Greenville soil (table 1). It may be that resistance to root penetration entails more than low macroporosity or even mechanical resistance to a probe or core sampler. Possibly the cementing of soil grains into a firm layer may prevent root penetration even though the soil may be adequately supplied with nutrients and is permeable to water and air. Reasons for the variations in effects of deep tillage at different locations will be better understood as more is learned about the physical properties of the soils.

SUMMARY

Several seedbed preparation methods, varying chiefly in depth of tillage, were compared as to their effect on soil and cotton plant characteristics on two Alabama soils, Greenville fine sandy loam and Decatur clay. Although differences in soil characteristics due to treatment were evident, the results were not significant or were inconclusive in regard to the effect of single treatments on plant characteristics. The treatments were grouped on the basis of tillage depth (deep—more than 7 inches; medium—5-7 inches; shallow—less than 5 inches) and analyzed for significance between treatment mean differences. Relative depth of rooting increased with tillage depth on both soils. For the Greenville soil, yields were highest on the deep-tilled plots but the effect on plant height was small. Tillage depth seemed to have little effect on the yields or plant heights on the Decatur soil.

REFERENCES

- (1) AASHEIM, T. S. 1949 Effect of tillage method on soil and moisture conservation and on yield and quality of spring wheat in the plains area of northern Montana. Mont. Agr. Exp. Sta. Bul. 468.

- (2) BOWER, C. A., BROWNING, G. M., AND NORTON, R. A. 1945 Comparative effects of plowing and other methods of seedbed preparation on nutrient element deficiencies in corn. *Soil Sci. Soc. Amer. Proc.* (1944) 9: 142-146.
- (3) BRASHER, E. P. 1949 Effect of plowing and of discing soils on the yield of tomatoes, muskmelons and potatoes. *Amer. Soc. Hort. Sci. Proc.* (1948) 51: 357-358.
- (4) CARDON, P. V. 1915 Tillage and rotation at Mephi, Utah. U. S. Dept. Agr. Bul. 157.
- (5) CHEPIL, W. S. 1946 Germination of weed seeds; the influence of tillage treatment on germination. *Sci. Agr.* 26: 347-57.
- (6) CHILCOTT, E. C., AND COLE, J. S. 1918 Subsoiling, deep tilling and dynamiting in the Great Plains. *Jour. Agr. Res.* 14: 481-521.
- (7) DULEY, F. L., AND RUSSELL, J. C. 1943 Effect of stubble mulching on soil erosion and runoff. *Soil Sci. Soc. Amer. Proc.* (1942) 7: 77-88.
- (8) HEATH, O. V. S. 1937 Study in soil cultivation, the effects of varying soil consolidation on growth and development of rain grown cotton. *Jour. Agr. Sci.* 27: 511-540.
- (9) HUME, A. N. 1943 Crop yields as related to depth of plowing. S. Dak. Agr. Exp. Sta. Bul. 369.
- (10) JAMISON, V. C., WEAVER, H. A., AND REED, I. F. 1950 A hammer-driven soil-core sampler. *Soil Sci.* 69: 487-496.
- (11) JAMISON, V. C., AND WEAVER, H. A. 1952 Soil hardness measurements in relation to soil moisture content and porosity. *Soil Sci. Soc. Amer. Proc.* (1951) 16: 13-15.
- (12) JONES, G. D. 1939 Method and effect of deep tillage. *Agr. Engin.* 20: 61-63.
- (13) LAWTON, K. 1946 Influence of soil aeration on the growth and absorption of nutrients by corn plants. *Soil Sci. Soc. Amer. Proc.* (1945) 10: 263-269.
- (14) LAWTON, K., AND BROWNING, G. M. 1949 Effect of tillage practices on the nutrient content and yield of corn. *Soil Sci. Soc. Amer.* (1948) 13: 311-317.
- (15) LILL, J. G. 1931 Plowing depths and fertilizers affect sugar beet crop. *Mich. Agr. Exp. Sta. Quart. Bul.* 13: 122-127.
- (16) LEONARD, O. A. 1945 Cotton root development in relation to natural aeration of some Mississippi delta soils. *Jour. Amer. Soc. Agron.* 37: 55.
- (17) MOSIER, J. G., AND GUSTAFSON, A. F. 1915 Soil moisture and tillage for corn. *Ill. Agr. Exp. Sta. Bul.* 181: 563-586.
- (18) NISSLEY, C. H. 1940 Our forgotten soil. *Country Gent.* 110 (2): 15.
- (19) OSBORN, W. M. 1932 Rotation and tillage experiments at the Lawton (Okla.) Field Station, 1917-1930. U. S. Dept. Agr. Tech. Bul. 330.
- (20) PAGE, J. B., WILLARD, C. J., AND MCCUEN, G. W. 1947 Progress report on tillage methods in preparing land for corn. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 78-80.
- (21) RANDOLPH, J. W., REED, I. F., AND GORDON, E. D. 1940 Cotton-tillage studies on Red Bay sandy loam. U. S. Dept. Agr. Cir. 540.
- (22) RUSSELL, E. W., AND KEEN, B. A. 1938 Studies in soil cultivation: VII. *Jour. Agr. Sci.* 28: 212-233.
- (23) RUSSELL, E. W., AND MEHTA, N. P. 1938 Studies in soil cultivation: VIII. *Jour. Agr. Sci.* 28: 272-298.
- (24) RUSSELL, E. W., AND KEEN, B. A. 1941 Studies in soil cultivation: X. *Jour. Agr. Sci.* 31: 326-347.
- (25) SARVIS, J. T., AND THYSELL, J. C. 1936 Crop rotation and tillage experiments at Northern Great Plains Field Station, Mandan, N. Dak. U. S. Dept. Agr. Tech. Bul. 536.
- (26) SMITH, R. S. 1925 Experiments with subsoiling, deep tilling and subsoil dynamiting. *Ill. Agr. Exp. Sta. Bul.* 258.
- (27) VEIHMEYER, F. J., AND HENDRICKSON, A. H. 1948 Soil density and root penetration. *Soil Sci.* 65: 487-493.
- (28) WOODRUFF, C. M., AND SMITH, D. D. 1947 Subsoil shattering and subsoil liming for crop production on claypan soils. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 539-542.
- (29) YATES, F. A. 1936 New method of arranging variety trials involving a large number of varieties. *Jour. Agr. Sci.* 26: 424-455.

POROUS TUBE DEVICE FOR SAMPLING SOIL SOLUTIONS DURING WATER-SPREADING OPERATIONS

RAY B. KRONE, H. F. LUDWIG, AND JEROME F. THOMAS

University of California

Received for publication August 3, 1951

Percolation of water through soil is a phenomenon involved in many sanitary engineering processes, such as the reclamation of sewage by spreading on porous ground, so that the water content of the sewage will percolate downward and augment underground water supplies, and in the disposal of septic tank effluents through subsurface leaching systems. The phenomena that occur along the path of the percolating water are of great importance and are being increasingly studied. Such studies require withdrawal of samples of the percolating water or soil solution at intervals along the soil profile.

Two common sampling methods are (a) use of pans placed in the soil to catch the downward moving water, and (b) removal of a sample of the soil, from which the soil solution may be displaced in the laboratory. Method (b) involves gross disturbance of the soil and hence is not suited to continuous investigations. Method (a), employed extensively in recent years,¹ has been found to have serious disadvantages, as follows: 1. Placement of the pans is difficult without disturbing the overlying soil, and it is difficult to obtain a good "bond" with the overlying soil; 2. The method fails when the percolating water is under tension;² 3. The flow path, and perhaps the characteristics of the percolating water, are seriously altered; 4. The size of the pans, if these are large enough to collect significant samples, limits the number that can be used, and hence makes it difficult to collect samples from enough locations to assure representative results.

This paper describes an improved sampling method developed by the Sanitary Engineering Research Project, which involves the use of a porous tube or "probe" to which negative pressures or tensions are applied. The method was investigated on the suggestion of P. R. Day of the department of soils, University of California, and is being applied to the project's current investigation of sewage reclamation by spreading.

THE METHOD

The porous tube or probe is inserted into the soil at the desired sampling depth. The tension or negative pressure necessary to withdraw the liquid may be provided by any means, but usually the most convenient method is to use a

¹ Arnold, C. E., Hedger, W. E., and Rawn, A. M. Report upon the reclamation of water from sewage and industrial wastes in Los Angeles County, California. [Unpublished report of Los Angeles Co. Sanit. Dists., April 14, 1949.]

Unpublished reports of studies on sewage reclamation by spreading. Sanit. Engin. Res. Proj., Univ. Calif. Berkeley (1950-51).

² These conditions are often found, especially in stratified soils.

"hanging" column of water or siphon, as illustrated in figures 1 and 2. Prior to sampling, the probe and connecting tubing must be completely filled with water to displace air and to establish the siphon. The yield of the sampling system is discarded until the water initially present in the probe and connecting tubing has been displaced.

SPECIFICATIONS FOR POROUS TUBES

The type of porous material best suited for probe construction has not been completely ascertained. Various types of probes were studied (fig. 3) in an attempt to determine what factors are significant in influencing the yield. It was found that the average porosity of the material is the most important criterion, and that the best porosity probably lies in the range of $1\ \mu$ to $10\ \mu$. Smaller pores were found to be readily clogged by fine particles, and large pores are apparently

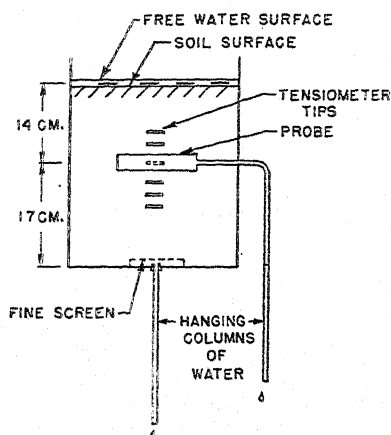


FIG. 1. SCHEMATIC DRAWING OF APPARATUS USED FOR STUDYING PROBE SAMPLING

filled in with a densely packed material.³ The proper pore size may be compared with the proper size of openings in a well screen; what is desired is a permeable and stable packing of the soil particles at the probe surface.

An attempt to minimize or eliminate the effect of clogging was made by surrounding the probe with fine sand. This proved impractical because the sand could not be put into place without admitting air, which subsequently caused "binding" or interference with the flow.

A second factor influencing probe behavior is its permeability, or ability to transmit water with a minimum of friction. Permeability, however, is not so important as porosity, because increased frictional resistance may be overcome

³ The degree of clogging at different porosities is indicated by the yields obtained, and also by curves of the type shown in figure 4, which are plots of changes in soil solution tension versus distance from the probe on a horizontal plane. Extrapolating such curves to a point representing the surface of the probe gives data indicating the total frictional resistance measured from the probe surface. This becomes greater with greater clogging.

by applying greater probe tensions. In any case, it is necessary to apply to the probe sufficient tension to overcome all of the frictional resistances involved plus the initial tension, if any, in the percolating water, such that the particles

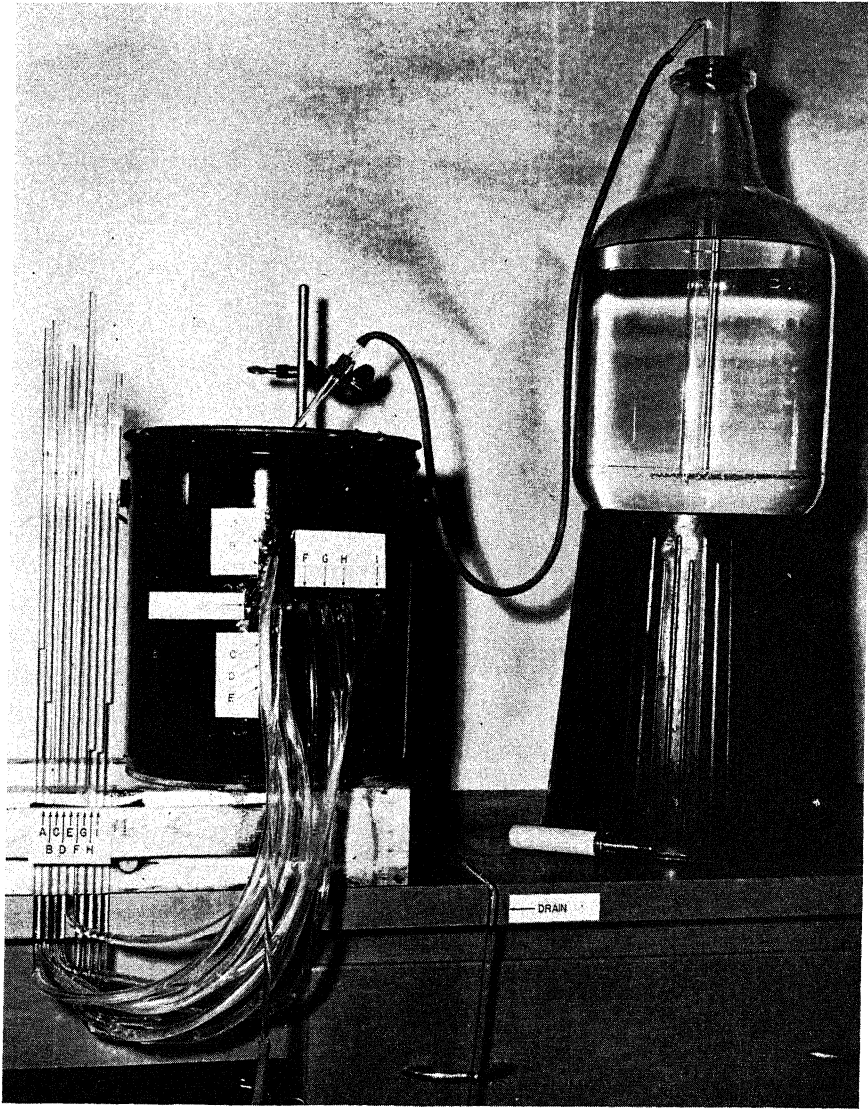


FIG. 2. APPARATUS USED FOR STUDYING PROBE SAMPLING

of water near the probe will flow toward and into the probe instead of continuing downward.

Permeabilities of porous materials are specified by their capacity to pass a given fluid through a unit area of the surface in unit time at a specified head,

for example, the amount of air at 75° F. and 24 per cent humidity passed in 1 minute through 1 square foot of the porous material under a head of 2 inches of water. The test data indicate that the porous material having the best permeability characteristics passes 0.2 to 0.4 cubic feet per minute per square foot under the specified conditions.⁴

Another important property of the porous material is its structural strength. The Mandler tube, which is 1 inch in outside diameter and 5 inches long, is the only commercially available type that incorporates an adapter for connecting to rubber tubing. It is commercially available only in very fine porosities, and upon continued use it becomes structurally weak and cannot safely be moved from one location to another. Carborundum tubes are strong and durable but are not commercially available with adapters, and hence must be specially made up.

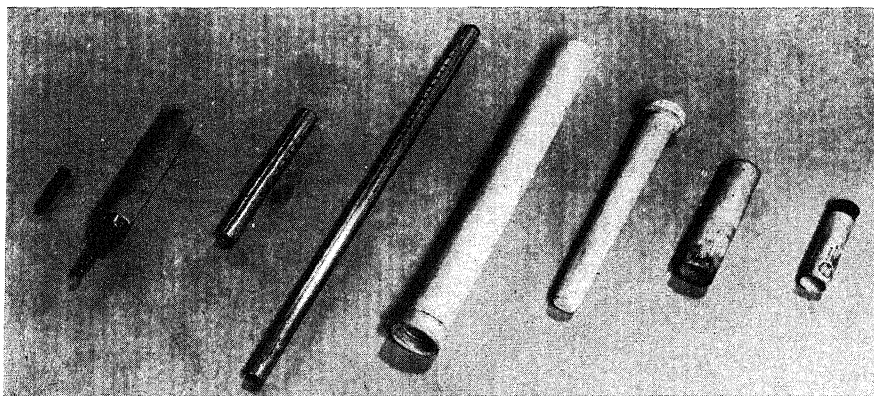


FIG. 3. TYPICAL PROBES TESTED

A 12-inch tube is probably the maximum practical length. Greater lengths can extract water from a greater soil volume or region, but the extra yields are relatively small.

HYDRAULICS OF SAMPLING

Test procedure

An investigation of the pattern of flow from the soil into the probe was made with a column of Yolo loam carefully packed in a container 30 cm. high and 28 cm. in diameter, with a Mandler 2-pound probe placed in a horizontal position at the center of the container, 14 cm. from the top (figs. 1 and 2). To measure the changes in pressure occurring in the soil solution as a result of the sampling, tensiometer tips⁵ were placed above, below, and to the side of the

⁴ The Mandler filter, such as used in the tests, is rated by the manufacturers on the basis of the pressure in psi. on the filter wall necessary to produce air leakage under water. A pressure of 0.5 to 1.0 psi. corresponds roughly to a permeability of 0.2 to 0.4 cu. ft. per minute.

⁵ A tensiometer tip is essentially a tiny probe connected to a manometer leg, which therefore measures the pressure existing in the soil solution at the location of the tip.

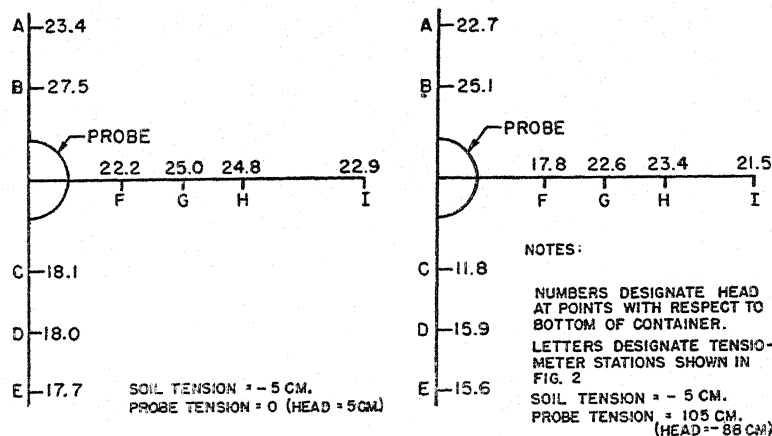


FIG. 4. POSITIONS OF TENSIO-METER TIPS AND RECORDED MEASUREMENTS
Scale: 1 inch = 2.5 inches

TABLE 1
*Soil solution head at various tensiometer stations**
In centimeters water above base of column
Initial solution pressure at probe = +5 cm.

TENSIO-METER STATION	TENSION APPLIED TO PROBE, IN CM. WATER				
	0	105	60	25	0
A	23.4	22.7	23.2	23.4	23.7
B	27.5	25.1	27.0	27.3	28.0
C	18.1	11.8	16.7	18.3	20.7
D	18.0	15.9	18.0	18.7	19.6
E	17.7	15.6	17.9	18.7	19.5
F	22.2	17.8	20.6	21.8	23.3
G	25.0	22.6	24.3	25.0	25.7
H	24.8	23.4	24.7	25.1	25.7
I	22.9	21.5	23.4	23.8	24.4

Initial solution pressure at probe = -10 cm.

TENSIO-METER STATION	TENSION APPLIED TO PROBE, IN CM. WATER			
	0	37.5	85	115
A	14.4	12.7	6.3	13.2
B	12.0	8.3	-2.1	-7.0
C	5.9	1.4	-12.4	—
D	4.3	2.8	-3.9	-9.1
E	3.4	2.1	-3.9	-6.9
F	7.2	-1.2	-20.5	—
G	9.1	6.1	-3.4	-7.5
H	8.5	7.4	-2.0	-1.4
I	11.0	9.3	4.9	1.4

* All tests made with a 2-pound Mandler filter having an estimated average pore size of 1μ .

probe, as shown in figure 4. Also, to control the downward flow through the column, the bottom of the column was subjected to tension in the manner described by Coleman.⁶

Two series of tests were made: first, with an initial solution tension of -5 cm., that is, with a positive pressure in the percolating liquid; and second, with an initial solution tension of 10 cm., representing a condition adverse to sampling by means of pans. In each series a number of different probe tensions were applied, and, after establishment of equilibrium in each case, the yield and solution pressure were recorded. The data on yields are shown in figure 5. The solution pressure data are presented in table 1, with the values corrected to refer to the bottom of the container as a reference datum. Diagrams illustrating a

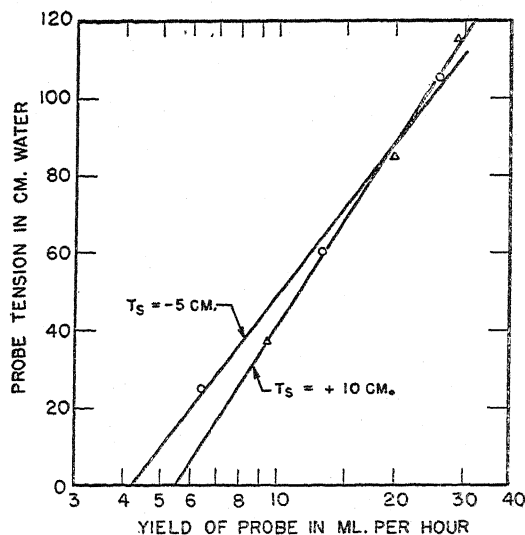


FIG. 5. YIELDS FOR VARIOUS PROBE TENSIONS

typical set of data are shown in figure 4. In figure 4 the numbers on the left are the solution pressures found when the probe is inoperative (closed off), and those on the right when 105-cm. probe tension is applied.

The data presented refer to only one soil type, and moreover were affected to some degree by nonuniformity in soil packing and by presence of the tensiometer tips. The results are believed, however, to be closely representative of actual field conditions.

Interpretations

The significance of the data is indicated by the change in solution pressure following application of the probe tension. Figure 6 illustrates, for example, the

⁶ Coleman, E. A. A laboratory study of lysimeter drainage under controlled soil moisture tensions. *Soil Sci.* 62: 365, 1946. The method applies tension to the base of the column, where otherwise water would accumulate in a "static mound." By varying the tension applied to the base, the initial soil solution pressures may be changed at will.

equilibrium solution pressures occurring on a vertical plane perpendicular to the probe, when the initial solution pressure is -5 cm. tension (5 cm. positive pressure) and the applied tension is 105 cm. The drawing, which is typical for

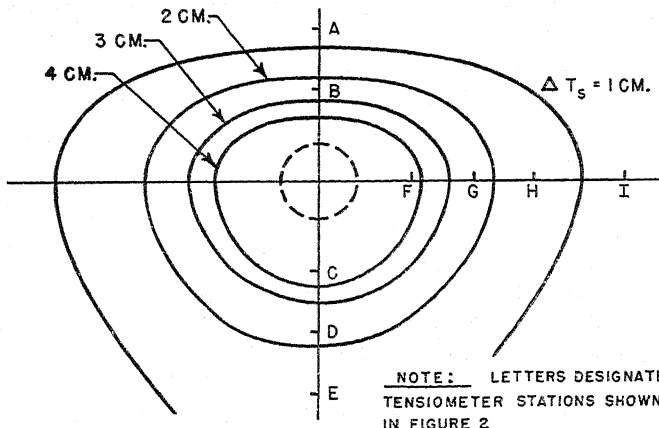


FIG. 6. CHANGES IN SOLUTION TENSIONS ON PLANE PERPENDICULAR TO PROBE
Scale: 1 inch = 2.5 inches

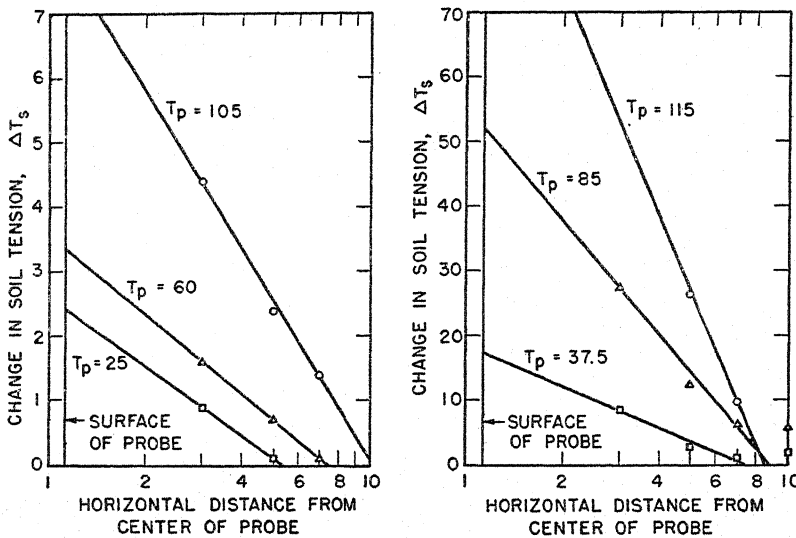


FIG. 7. CHANGES IN SOLUTION TENSION WITH RESPECT TO HORIZONTAL DISTANCE FROM PROBES

most combinations of conditions, shows that the locus for a given pressure change approximates an egg-shaped curve with its apex beneath the probe. Hence, the changes in pressure are greater below the probe than above.

The changes along a line of constant hydrostatic head, that is, on a horizontal line perpendicular to the probe, are illustrated in figure 7. The change in solu-

tion pressure approximates a logarithmic function of the distance from the probe, and is probably determined by the soil permeability and the initial solution pressure, as well as by the applied tension. If this curve is extrapolated to a point representing zero pressure change, the corresponding distance from the probe is still small. Thus, the applied probe tension disturbs the flow pattern in only a small or limited region, and the sampling process therefore results in negligible disturbance to the general flow pattern.

The yield of the probe (fig. 5) appears to be a logarithmic function of the applied probe tension for a given soil permeability and initial solution pressure. The greater the applied probe tension, the greater the yield (and the greater the volume of the region disturbed), but the increase in yield with increase in applied tension becomes progressively less. The yield is small, about 20 ml. per hour, but is sufficient for most analytical testing.

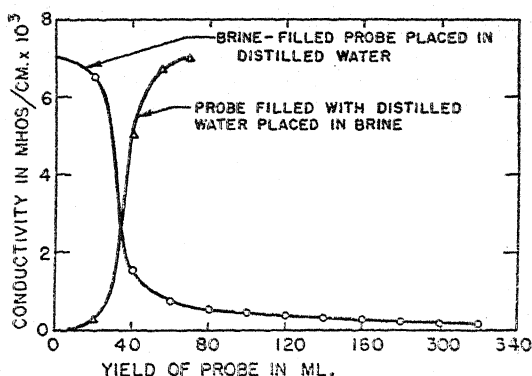


FIG. 8. DISPLACEMENT OF LIQUID FROM PROBE

Miscellaneous techniques

As previously noted, prior to sampling it is necessary to fill the probe and connecting tubing with water, eliminating all air bubbles. This may be readily accomplished by pumping water into the probe, with a hand syringe, until water flows from the probe to the soil.

After the probe is operating, the initial water must be displaced and discarded before proper samples will be delivered. To determine how much displacement is necessary, tests were made with a probe filled with distilled water immersed in NaCl brine and again with a probe filled with brine immersed in distilled water, by measuring the electrical conductivity of the effluent delivered by the probe; with enough applied probe tension to produce a flow of 20 ml. per hour. The results are shown in figure 8, and indicate that the volume to be displaced and discarded before sampling is closely equal to the volume of the probe and its associated tubing.

The probe tension may be applied by use of a vacuum pump instead of a hanging water column. With a vacuum pump, the flow is irregular but over a period of time averages the same as with a hanging column.

CONCLUSIONS

The probe is a convenient sampling device that extracts water from the soil by forming a hydrodynamic sink. The configuration of the hydraulic flow and pressures in a vertical plane are similar to those existing around the perforated zone of a well into which underground water is flowing. The magnitude of the tension applied to the probe is so small, however, that the volume or region of soil affected is very small, extending only about 10 cm. from the probe for applied probe tensions of about 100 cm. Thus the disturbance caused by the sampling scarcely affects the general pattern of flow through the soil.

The proper tension to be applied to the probe will depend upon the soil permeability, the permeability of the probe material, the frictional resistance in the connecting tubing, and the initial soil solution pressure. The necessary probe tension is readily applied by means of a hanging water column.

With a proper probe porosity and length, the feasible yield per probe is about 20 ml. per hour.

FREEZING POINT OF WATER IN PUDDLED AND UNPUDDLED SOILS AT DIFFERENT SOIL MOISTURE TENSION VALUES

ROBERT B. CAMPBELL

U. S. Department of Agriculture¹

Received for publication May 14, 1951

A satisfactory measuring technique that will indicate the physical condition of water in the soil has long been sought by scientists. The method should include the effect of soluble materials on the osmotic pressure of the soil solution, and also the effect of surface force action between the soil and the soil water.

The cryoscopic procedure used by Parker (6) indicates the adaptability of this method for measuring the tenacity with which water is held by soil. Following Parker's work, Schofield and Da Costa (14) and Bodman and Day (2) used the freezing point method to describe the physical condition of soil water at the moisture equivalent. The freezing point of soil moisture in the plant wilting range has been measured by a number of workers (1, 2, 12, 13, 14, 16).

Richards and Weaver (7) have shown that soils placed on porous membranes have a unique moisture content corresponding to the differential pressure applied across the membrane. Under these equilibrium conditions the soil moisture tension is said to be equal to the pressure difference across the membrane, regardless of the texture or structural condition of the soil. Freezing points obtained in soil at constant soil moisture tension do not appear to be independent of textural and structural soil conditions. The purpose of this study is to show the magnitude of these textural and structural variations on the observed freezing point at several soil moisture tension levels. Several freezing treatments were included in this study to investigate improvements in the freezing technique. In addition, each soil sample was frozen, thawed, and refrozen five times to investigate the decrease in the observed freezing point between successive freezings.

EXPERIMENTAL PROCEDURE

Three soil types were selected to represent a textural range for mineral soils. Each soil was air-dried, passed through a 2-mm. round-hole sieve, and subdivided into eight pint jars. Half of the soil samples were brought approximately to field capacity by addition of water and were then stirred with a rod to obtain a high degree of puddling. These soils were saturated with water and transferred to porous membranes. The remaining four subsamples of unpuddled soil were poured on porous membranes and were saturated by applying water to the upper soil surface. Pressures of $\frac{1}{3}$, 1, 5, and 15 atmospheres were applied to separate membranes. These pressure values are reported as soil moisture tension. Ceramic

¹ Joint contribution from the U. S. Salinity Laboratory, where the experimental work was done, and the department of agronomy, Utah State Agricultural College, where the results were presented to the Graduate School in partial fulfillment of the requirements for the degree of master of science. The author is indebted to L. A. Richards for advice and assistance on the work presented in this paper.

plates (10) were used for the $\frac{1}{3}$ to 1 atmosphere pressure range, and cellulose membranes (8) were used above 1 atmosphere. When water flow through the porous membranes ceased, the cells were dismantled. Disks of soil were cut and

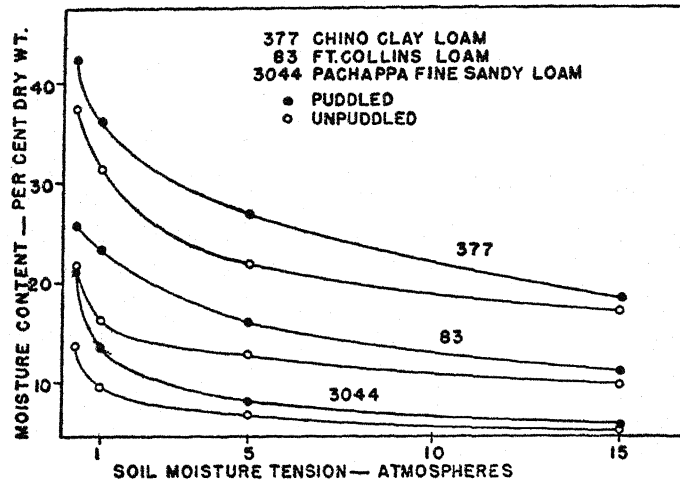


FIG. 1. SOIL MOISTURE TENSION CURVES FOR THREE SOILS IN PUDDLED AND UNPUDDLED CONDITION

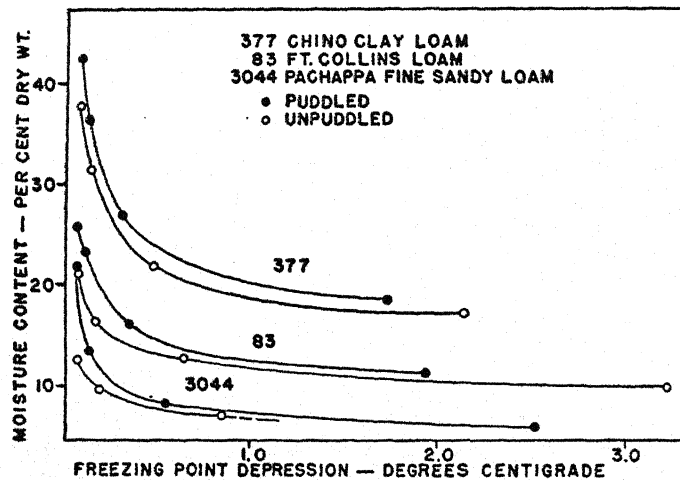


FIG. 2. RELATION OF FREEZING POINT DEPRESSION TO MOISTURE CONTENT FOR THREE SOILS IN PUDDLED AND UNPUDDLED CONDITION

stacked into small, thin-walled, hard-rubber cylinders. These core containers were capped and placed in $\frac{3}{4}$ -inch glass test tubes, which were closed with rubber stoppers to prevent moisture loss before freezing. The freezing procedure and freezing equipment used in this study have been described (9, 11).

The fifteen core samples cut from the soil on the pressure membrane at four

tension levels were randomized into three groups of five cores each. These cores were subjected to a "normal freeze," a "deep freeze," and an "adiabatic freeze." In the "normal freeze" process, the cores were undercooled 1.0 to 1.5°C. below the expected freezing point. Freezing was initiated, and the observed temperature

TABLE 1
Osmotic pressure of solution extracted from saturated soil paste

SOIL NUMBER	SOIL TYPE	SATURATION PERCENTAGE	ELECTRICAL CONDUCTIVITY (EC)	OSMOTIC PRESSURE (OP)*
			<i>millimhos/cm.</i>	<i>atmosphere</i>
3044	Pachappa fine sandy loam	29	1.20	0.39
83	Ft. Collins loam	42	0.76	0.24
377	Chino clay loam	62	0.98	0.31

* OP was calculated from the equation (5): $OP = 0.321 \times (EC \times 10^3)^{1.055}$.

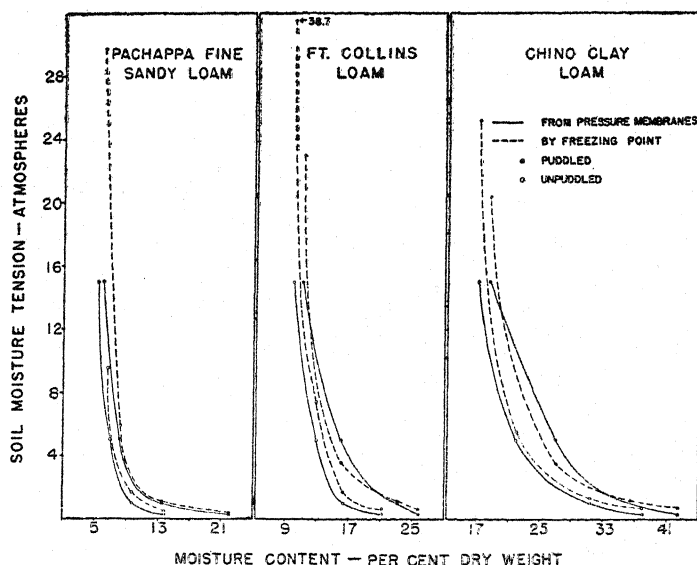


FIG. 3. PERCENTAGE-WATER-SOIL-MOISTURE-TENSION CURVES OBTAINED FROM PRESSURE MEMBRANES AND FREEZING POINT DATA

The dotted curves were obtained from freezing point values, ΔT_0 , as follows: soil moisture tension = $12.06 \Delta T_0 - OP$, where OP is the osmotic pressure of the soil solution.

maxima during freezing were recorded. The difference between the temperature maxima and the ice point is referred to as the observed freezing point depression, ΔT_0 . The samples given the "deep freeze" treatment were frozen initially by the "normal freeze" procedure and immediately transferred to a deep freeze unit at -20°C . After 3 hours the samples were transferred from the deep freeze unit to a bath at 0°C . for thawing. All subsequent freezings of these soil cores were completed by the normal freezing procedure. For the "adiabatic freeze," the tem-

perature difference between the sample and its surroundings was kept small to minimize heat loss from the sample during freezing. To accomplish this, the core was undercooled, freezing was initiated, and the sample was then transferred to a bath previously adjusted to the expected freezing point.

Five successive freezings and thawings were made on all cores prepared for the

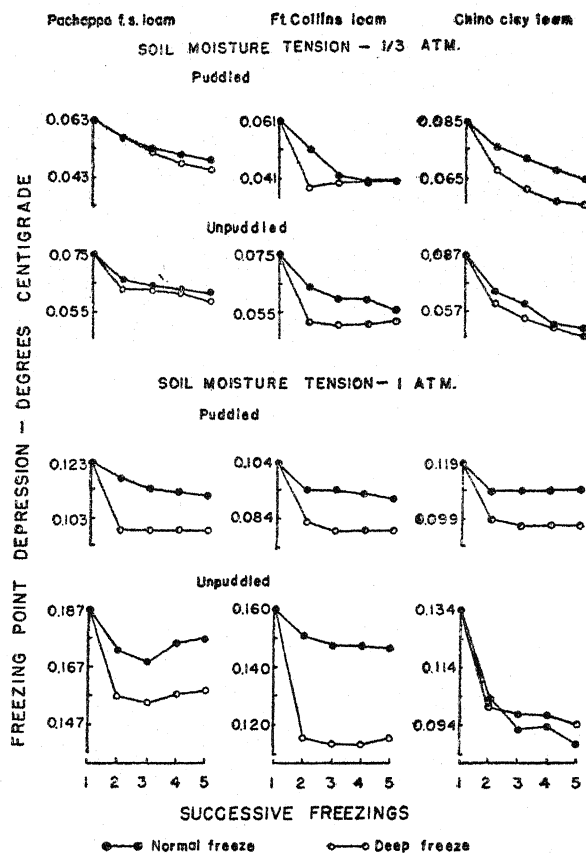


FIG. 4. EFFECT OF ALTERNATE FREEZING AND THAWING ON THE FREEZING POINT DEPRESSION OF SOIL AT $\frac{1}{3}$ AND 1 ATMOSPHERES OF SOIL MOISTURE TENSION

study. These cores were thawed and stored in an ice bath between freezings to minimize thermal movement of moisture within the soil.

EXPERIMENTAL RESULTS

Soil moisture tension is plotted against soil moisture percentage in figure 1. At a given tension level, Pachappa fine sandy loam contains less water per unit mass than either Ft. Collins loam or Chino clay loam. Unpuddled soil contains less water than puddled soil at corresponding soil moisture tension levels.

Figure 2 shows the relationship between soil moisture content and the observed freezing point. The left point in each curve in the figure was obtained at the $\frac{1}{3}$

atmosphere soil moisture tension level. The second, third, and fourth points are fixed by freezing point data taken in soil at moisture equilibrium at 1, 5, and 15 atmospheres of soil moisture tension. Puddled soil gave smaller freezing point depression values than unpuddled soil at the same soil moisture tension.

The osmotic pressure (OP) of soluble salts for each soil is given in table 1. These osmotic pressure values were calculated from the electrical conductivity

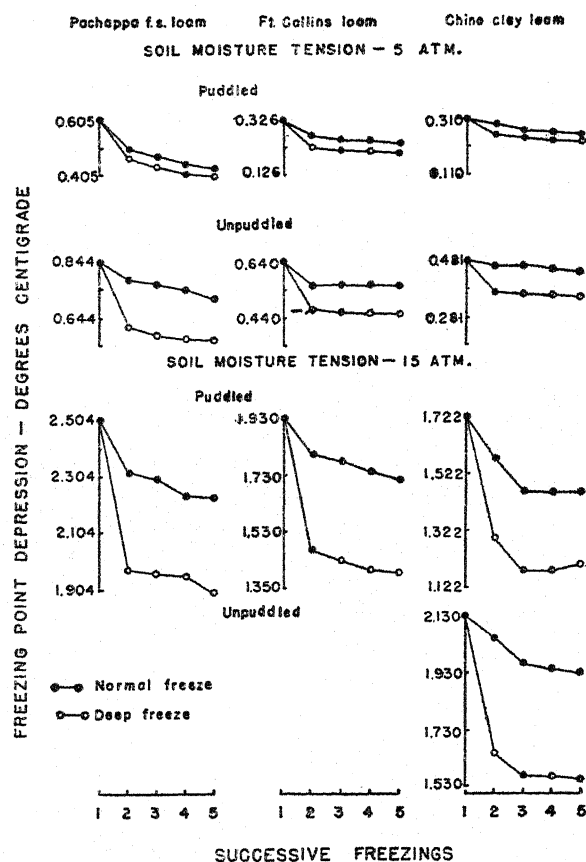


FIG. 5. EFFECT OF ALTERNATE FREEZING AND THAWING ON THE FREEZING POINT DEPRESSION OF SOIL AT 5 AND 15 ATMOSPHERES OF SOIL MOISTURE TENSION

of a soil extract obtained from a saturated soil paste. The conversion of freezing point depression (FPD) to soil moisture tension was made by subtracting the osmotic pressure values given in table 1 from the quantity $12.06 \times \Delta T_0$. In making this conversion, it is assumed that the concentration of soluble salts in the soil solution did not change during the extraction process on the porous membranes. Soil moisture tension values obtained by subtraction are plotted in figure 3 against the soil moisture percentage. Soil moisture tension obtained on the porous membrane apparatus is also plotted against moisture content.

In figure 3 the percentage-water-soil-moisture-tension curves obtained by the

freezing point lie to the right of the curve obtained by use of porous membranes, except for the 5-atmosphere soil moisture tension points for Ft. Collins loam and Chino clay loam. The puddled moisture tension curves also lie to the right of curves obtained on porous membrane apparatus. Chino clay loam gave smaller observed freezing point depression values than either Ft. Collins loam or Pachappa fine sandy loam at corresponding soil moisture tension values.

TABLE 2

Standard error, SE, of the freezing measurements at several soil moisture tension levels

SOIL TYPE	FREEZING MEASUREMENTS							
	1/3 atm.		1 atm.		5 atm.		15 atm.	
	P*	Unp.†	P	Unp.	P	Unp.	P	Unp.
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Pachappa fine sandy loam								
FPD‡.....	0.063	0.075	0.124	0.180	0.527	0.844	2.504	—
SE.....	0.002	0.003	0.006	0.014	0.053	0.058	0.133	—
Ft. Collins loam								
FPD.....	0.062	0.075	0.104	0.164	0.326	0.640	1.930	—
SE.....	0.006	0.007	0.003	0.007	0.025	0.029	0.044	—
Chino clay loam								
FPD.....	0.085	0.087	0.119	0.134	0.310	0.481	1.722	2.130
SE.....	0.007	0.009	0.004	0.005	0.007	0.007	0.066	0.092
Av. Std. Error.....	0.005	0.006	0.004	0.008	0.028	0.031	0.081	0.092
Av. Std. Deviation.....	0.019	0.024	0.017	0.032	0.109	0.120	0.314	0.357
Av. FPD.....	0.070	0.079	0.116	0.159	0.414	0.653	2.052	2.117
Coefficient of variability...	26.7	30.9	14.4	20.1	26.6	18.4	15.3	16.8

* P = puddled soil.

† Unp. = unpuddled soil.

‡ FPD = freezing point depression.

Average observed freezing point depression values for soil frozen adiabatically were not significantly different from values obtained in soil cores frozen by the normal method. To obtain this result, the thermal time constant of the Thermistor,² in water, was about 2 to 4 seconds, which gives an indication of the low thermal capacity of the temperature-sensitive element used to measure the freezing point of soil. Usually the time required to obtain a measurable temperature change at the Thermistor, in response to a change in temperature of the core surroundings, was 1 to 2 minutes. This time depends mainly upon the thickness and type of insulation about the soil core and the thermal diffusivity of the soil.

² The Thermistor used was a Western Electric Type 14B. The Thermistor resistance minima observed during freezing were recorded and converted to temperatures from a previously determined calibration curve.

The effect of alternate freezing and thawing on the freezing point depression is shown in figures 4 and 5. Larger decreases in the freezing point depression were observed between the first and second successive freezings than between any other pair of successive freezing values. These results are in agreement with data reported by Bouyoucos and McCool (3), Schofield and Da Costa (15), and Buehler and Rose (4). Between the first and second freezing, soils given the deep-freeze treatment showed larger decreases in the freezing point depression than did soils frozen by the normal procedure. Half of the successive freezing curves show a gradual decrease in the freezing point depression after the initial freeze, whereas, the remaining half show no change or a slight increase as a result of additional freezings. The decreases in the freezing point depressions after the initial freezing were greater at the high soil moisture tension levels than at low tension levels.

The freezing point depression values and the standard error in degrees centigrade for puddled and unpuddled Chino clay loam, Ft. Collins loam, and Pachappa sandy loam at several soil moisture tension levels are given in table 2. The average standard error for the soils tested over the moisture tension range considered here varies between 0.005 and 0.092°C. The coefficients of variability for soils in the $\frac{1}{3}$ - to 15-atmosphere pressure range vary from 30.9 to 14.4 per cent.

DISCUSSION

The differences between the calculated and the actual soil moisture tension curves probably arise from assumptions connected with the osmotic pressure calculation and also from the fact that no undercooling correction was made on the observed freezing point depression. Errors from both of these sources tend to increase at low moisture, high tension levels.

Bodman and Day (2) and Schofield and Da Costa (15) have calculated an undercooling correction to be applied to the observed freezing point. The effect of undercooling on the observed freezing point was experimentally studied by the author for a number of soils in the tension range from 5 to 15 atmospheres and in the undercooling range from 0.3 to 3.0°C. The change in ΔT_0 with undercooling was small for the soils tested and sometimes was in the opposite direction to the change predicted by the theory. In view of these contradictory results, no undercooling correction was applied to the experimental data reported herein.

For the experimental technique used, the average observed freezing point values for soil cores frozen by the normal method at the undercooled temperature were essentially the same as for cores frozen adiabatically in a bath adjusted to the expected freezing point. Precautions associated with the adiabatic freezing technique are made unnecessary by surrounding the soil sample with adequate thermal insulation and by reducing the heat capacity and the thermal lag of the temperature-sensitive element used in the freezing measurement.

In the successive freezing study it was observed that larger decreases occur between the first and second freezings than between any two later freezings. This decrease in the freezing point depression may be due to a decrease in the "mechanical resistance" of soil to ice crystal formation. In other words, during later freezings, ice may reform in cavities that were produced during the earlier freezings. Also it is possible that a change of soil structure may occur which causes

some water to be held less securely by the soil after freezing and thawing. Both of these effects may cause the observed change in freezing point depression with successive freezing.

SUMMARY

Three soils, in puddled and unpuddled condition, were brought to equilibrium on porous membranes at known soil moisture tension values. Pachappa fine sandy loam, Ft. Collins loam, and Chino clay loam contained higher percentages of water (oven-dry basis) at the same soil moisture tension level in a puddled condition than in an unpuddled condition in the soil moisture tension range from $\frac{1}{3}$ to 15 atmospheres. These same soils gave freezing point depression values which were larger in the puddled sample than in an unpuddled sample at the same moisture content. Clay loam soil gave smaller observed freezing point depression values than did loam or fine sandy loam soils at the same soil moisture tension.

The average observed freezing point depression values for soil cores frozen by the usual procedure at the undercooled temperature were the same as those for cores frozen adiabatically in a bath adjusted to the expected freezing point.

Soil moisture tension expressed in atmospheres was calculated from freezing point depression data by subtracting the osmotic pressure of the soil solution from $12.06 \times \Delta T_0$, where ΔT_0 represents the observed freezing point depression. These calculated soil moisture tension data were plotted against moisture content and compared at the same moisture content with soil moisture tension values obtained on a pressure membrane.

Larger decreases in the freezing point depression were observed between the first and second freezing than between any two later freezings.

REFERENCES

- (1) BLAIR, G. Y., RICHARDS, L. A., AND CAMPBELL, R. B. 1950 Rate of elongation of sunflower plants and the freezing point of soil moisture in relation to permanent wilt. *Soil Sci.* 70: 431-439.
- (2) BODMAN, G. B., AND DAY, P. R. 1942 Freezing points of a group of California soils and their extracted clays. *Soil Sci.* 55: 225-246.
- (3) BOUYOUCOS, G. J., AND MCCOOL, M. M. 1916 Further studies on the freezing point lowering of soils. Mich. Agr. Exp. Sta. Tech. Bul. 31.
- (4) BUEHRER, T. F., AND ROSE, M. S. 1943 Studies in soil structure: V. Ariz. Agr. Exp. Sta. Tech. Bul. 100.
- (5) CAMPBELL, R. B., BOWER, C. A., AND RICHARDS, L. A. 1949 Change of electrical conductivity with temperature and the relation of osmotic pressure to electrical conductivity and ion concentration for soil extracts. *Soil Sci. Soc. Amer. Proc.* (1948) 13: 66-69.
- (6) PARKER, F. W. 1921 Effect of finely divided material on the freezing point of water, benzene and nitrobenzene. *Jour. Amer. Chem. Soc.* 43: 1013-1018.
- (7) RICHARDS, L. A., AND WEAVER, L. R. 1944 Moisture retention by some irrigated soils as related to soil moisture tension. *Jour. Agr. Res.* 69: 215-235.
- (8) RICHARDS, L. A. 1947 Pressure membrane apparatus—construction and use. *Agr. Engin.* 28: 451-454.
- (9) RICHARDS, L. A., AND CAMPBELL, R. B. 1948 Use of Thermistors for measuring the freezing point of solutions and soils. *Soil Sci.* 65: 429-436.

- (10) RICHARDS, L. A. 1949 Methods of mounting porous plates used in soil moisture measurements. *Agron. Jour.* 41: 489-490.
- (11) RICHARDS, L. A., AND CAMPBELL, R. B. 1949 Freezing point of moisture in soil cores. *Soil Sci. Soc. Amer. Proc.* (1948) 13: 71-74.
- (12) RICHARDS, L. A., CAMPBELL, R. B., AND HEALTON, L. W. 1950 Some freezing point depressions on cores of soil in which cotton and sunflower plants were wilted. *Soil Sci. Soc. Amer. Proc.* (1949) 14: 47-50.
- (13) ROBERTSON, L. S., AND KOHNKE, H. 1947 pF at the wilting point of several Indiana soils. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 50-53.
- (14) SCHOFIELD, R. K., AND DA COSTA, J. V. B. 1935 Determination of the pF at permanent wilting and at the moisture equivalent by the freezing point method. *Trans. Third Internatl. Cong. Soil Sci.* 1: 6-10.
- (15) SCHOFIELD, R. K., AND DA COSTA, J. V. B. 1938 Measurement of the pF in soil by freezing point. *Jour. Agr. Sci.* 28: 644-652.
- (16) VEIEMEYER, F. J., AND HENDRICKSON, A. H. 1950 Methods of measuring field capacity and permanent wilting percentages of soils. *Soil Sci.* 68: 75-94.

USE OF TOTAL YIELD FOR PREDICTING NITROGEN CONTENT OF INOCULATED LEGUMES GROWN IN SAND CULTURES

LEWIS W. ERDMAN AND URA MAE MEANS¹

U. S. Department of Agriculture

Received for publication August 2, 1951

The effectiveness of pure cultures of legume bacteria and legume inoculants on different legumes is generally measured by color differences, height of plants, length of roots, degree of nodulation, dry weight of entire plant, and nitrogen content. In some experimental work three to eight replicates are used for each inoculum. The task of making total nitrogen determinations on all these samples is expensive and tedious. Inoculated legumes grown in sand cultures under controlled conditions in the greenhouse show a marked uniformity in percentage of nitrogen, regardless of the inoculant used. It has been observed, furthermore, that the dry weight of a given number of plants from sand cultures bears a close relation to the total amount of nitrogen recovered by analysis. In view of these facts, the question is raised concerning the necessity of running nitrogen analyses on samples from different experiments. Could mathematical formulas be used to predict nitrogen content?

Wilson, Hopkins, and Fred (6) found that the limit of nitrogen fixed by red clover in agar is a function of the growth of the plants. Wilson, Wenck, and Peterson (7) made a statistical study of nitrogen fixation by clover plants. The variables studied were milligrams nitrogen fixed; number, type, and location of nodules; number of leaves; length of stems and length of roots. The simple correlation coefficients indicated that no two of these variables were highly correlated with each other. Because of these low correlations, knowledge of the magnitude of one of these variables gave little information concerning the corresponding magnitude of another variable. The correlation coefficients were lower in the agar series than in the sand cultures. Although the data indicate that more nitrogen was fixed by the stockier plants, yield or dry weight was not taken, consequently the relationship between amount of nitrogen fixed and total dry weight was not studied.

Georgi (4) combined data from 10 experiments and determined the correlation coefficients between the number of nodules and percentage of nitrogen. He found a decidedly significant negative correlation between percentage nitrogen and number of nodules. Allam (1) grew soybeans and determined the nitrogen content and dry weight of controls and inoculated plants. From these data the theoretical dry weights of the inoculated plants were predicted by using Mitscherlich's formula. Allam reported that the law of growth factors was only conditionally applicable to his problem because the plants did not grow to maturity. He was primarily interested in the energy required for fixation of nitrogen.

¹ The authors acknowledge the assistance of E. J. Koch of the Biometrical Services in the computations and interpretation of the data in this paper. The nitrogen determinations were made by E. M. Roller.

If the relationship between the amount of nitrogen fixed and total yield was such that the nitrogen content could be predicted from total yield, the time-consuming and expensive task of determining total nitrogen could be reduced. Accordingly, the work reported herein was undertaken to study the relationship between total dry weight and the nitrogen content of inoculated and uninoculated legumes grown in greenhouse sand cultures under controlled conditions and to determine whether nitrogen content could be predicted with reasonable accuracy from total dry weight.

METHODS

Data were available in this laboratory on 398 sand cultures of various legume species and varieties on which both total yield and nitrogen determinations had been made. The sand cultures were grown according to the regular assembly technique adopted by this laboratory (2). The majority of sand cultures were inoculated with single strains of pure cultures of rhizobia, and in most cases three replicates of each treatment were available. Total nitrogen was determined by a modified Kjeldahl method.

Preliminary consideration of the data indicated that a linear relationship existed between total yield and the amount of nitrogen. Standard regression and correlation methods as outlined by Snedecor (5) were followed. The constants evaluated have been described in detail by Fireman and Wadleigh (3).

RESULTS

A summary of the data obtained for alfalfa, sweet clover, bur clover, bitter clover, black medic, three varieties of soybean, and three species of lupines is presented in table 1. The statistical constants were calculated from individual values. Although the correlation coefficients presented were calculated from total variances and covariances, the coefficients calculated for strains and error variances and covariances were equally high.

The mean dry weight, as well as the amount of nitrogen recovered, varied considerably within each of the legumes. This was to be expected because of variations in individual plant characteristics and the differential efficiencies of the strains of rhizobia used. Further variation would be influenced by the length of the growing period and the season of the year.

The relative number of samples had no effect on the magnitude of the coefficients of correlation between total dry weight and nitrogen recovered. There were three times as many alfalfa samples as of sweet clover, yet the correlation coefficient was 0.99 in each case. Eighteen samples for each of the three species of lupines showed the same correlation coefficient, 0.98. The coefficient of correlation between the dry weight and total nitrogen is unusually high and deviates markedly from the over-all 0.97 average in only two cases, bur clover and Ogden soybeans. Even with these two legumes the coefficient of correlation is highly significant.

These highly significant correlations indicate a close linear relationship. Consequently the prediction equation

$$Y = \bar{y} + b_{y,x}(X - \bar{x}) \quad (1)$$

can be used with reasonable accuracy for estimating nitrogen content from total dry weight.

The r^2 (100) values, coefficients of determination, further show the accuracy of these predictions. With alfalfa, 98.5 per cent of the variation in nitrogen content is associated with concomitant variation in dry weight, or, in other words, nearly all of the variation in nitrogen is related to dry weight.

In bur clover, only 83.2 per cent of the variance in nitrogen is related to dry weight. The yields of two sand cultures of bur clover was exceptionally high with a corresponding low percentage of nitrogen. This could be explained by plant variation, especially since the cultures represented only one replication from two

TABLE 1

Mean dry weights and nitrogen contents of different legumes and statistical constants relating to these characters

LEGUME	NUM- BER OF SAM- PLES	DRY WEIGHT MEAN SAMPLE \bar{x}	NITROGEN RECOV- ERED MEAN SAMPLE \bar{y}	COEFFI- CIENT OF COR- RELATION r	COEFFI- CIENT OF DE- TERMINATION r^2 (100)	COEFFI- CIENT OF REGRES- SION $b_{y,x}$	STANDARD ERROR OF REGRES- SION CO- EFFICIENT $SEb_{y,x}$	STAND- ARD ERROR OF ESTIMATE $s_{y,x}$	STANDARD ERROR OF ESTIMATE OVER MEAN $RE_{y,x}$
		gm.	mgm.		per cent			mgm.	per cent
Alfalfa.....	69	17.48	521.57	.992	98.5	30.74	0.38	28.75	5.5
Sweet clover.....	21	19.38	662.50	.993	98.7	35.15	0.93	42.44	6.4
Bur clover.....	20	10.01	290.52	.912	83.2	32.88	2.86	94.88	32.7
Bitter clover.....	15	16.11	387.78	.982	96.4	24.13	1.31	42.35	10.9
Black medic.....	30	5.58	161.60	.996	99.1	29.41	0.58	9.21	5.7
Soybeans									
Ralsoy.....	57	9.06	197.99	.979	95.8	23.01	0.64	26.82	13.5
Ogden.....	93	5.41	122.96	.892	79.6	39.67	2.10	19.34	21.1
Peking.....	39	7.51	152.80	.983	96.6	22.70	0.70	18.56	12.1
Lupines									
Bitter blue.....	18	10.30	315.76	.988	97.7	35.22	1.35	25.80	8.2
Bitter yellow.....	18	7.30	237.75	.984	96.8	42.85	1.95	20.74	8.7
Sweet yellow.....	18	6.15	206.57	.986	97.1	37.93	1.54	26.05	12.6

different inoculants. These discrepancies made the standard error of estimate for bur clover extremely high as compared to the error for the other legumes.

The only other legume having a widely different coefficient of correlation and consequently lower coefficient of determination, was Ogden soybeans. This variety, though producing smaller yields, had a relatively high nitrogen content, and the slope of the regression line ($b_{y,x} = 39.67$) was much steeper than for the other two soybean varieties. With Ogden soybeans 79.6 per cent of the variation in nitrogen was related to dry weight. The remaining 20.4 per cent of the variation is not explainable by the data at hand.

The coefficient of regression value $b_{y,x}$, shows the change in milligrams in nitrogen content associated with a one-gram change in dry weight for each legume. The standard error of the regression coefficient $SEb_{y,x}$ when compared with the regression coefficient $b_{y,x}$, is indicative of the significance of $b_{y,x}$.

$$\text{The exact "t" test is } t = \frac{b_{y,x}}{SEb_{y,x}}$$

The standard error of estimate $s_{y,x}$ shows how closely the values estimated by the regression line agree with actually observed values of the variable being estimated. It is, essentially, the standard deviation of the y -variates from the regression line rather than from the mean.

An estimate of relative precision is given by the $RE_{y,x}$ values for the different legumes. In comparing these it is seen that bur-clover and Ogden soybean show the least precision.

For illustrative purpose data for the alfalfa sand cultures are plotted in figure 1. Dry weights are plotted on the x -axis, and the nitrogen content is plotted on the y -axis. The regression line is drawn through the y -intercept $(0, y)$ and the

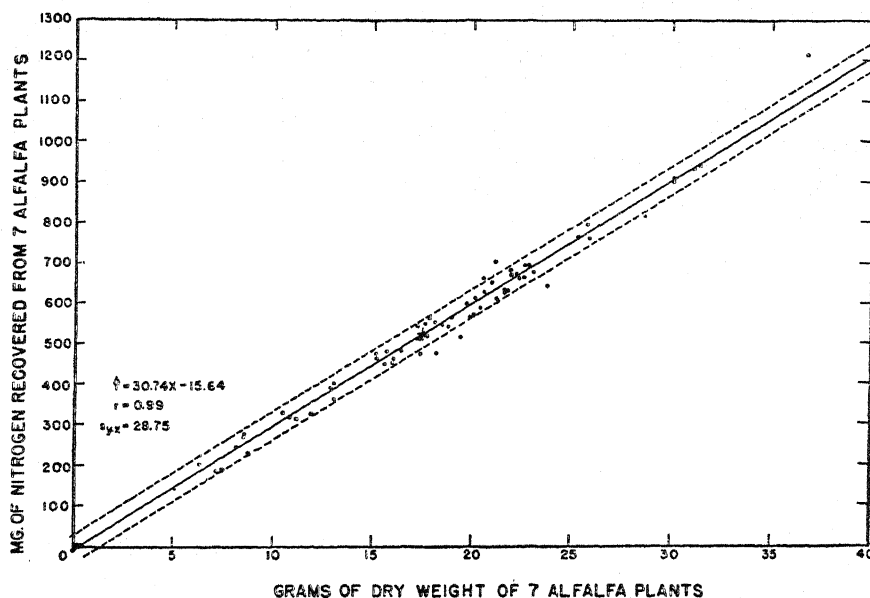


FIG. 1. REGRESSION OF NITROGEN CONTENT OF ALFALFA ON TOTAL YIELD

point (\bar{x}, \bar{y}) . The broken lines represent the regression line \pm the standard error of estimate (28.75 mgm.). Theoretically about 68 per cent of the points may be expected to fall within these broken lines. The closer the broken lines to the regression line, the higher is the precision of prediction. The prediction equation for alfalfa is obtained by substituting values from table 1 in equation (1). The resulting equation is

$$\hat{Y} = 30.74X - 15.64$$

By substituting the dry weight (X) for any individual alfalfa sand culture in the above equation the nitrogen content of that sample can be estimated.

The data from the other legumes were also plotted. As expected from the constants given in table 1, rather close agreement to the regression line was observed for the other legumes. Only bur clover showed a poor fit, and reasons for its variation have been discussed. From the constants for each legume, the amount

of nitrogen could be predicted from the dry weight of a given sample within the limits of accuracy shown.

DISCUSSION

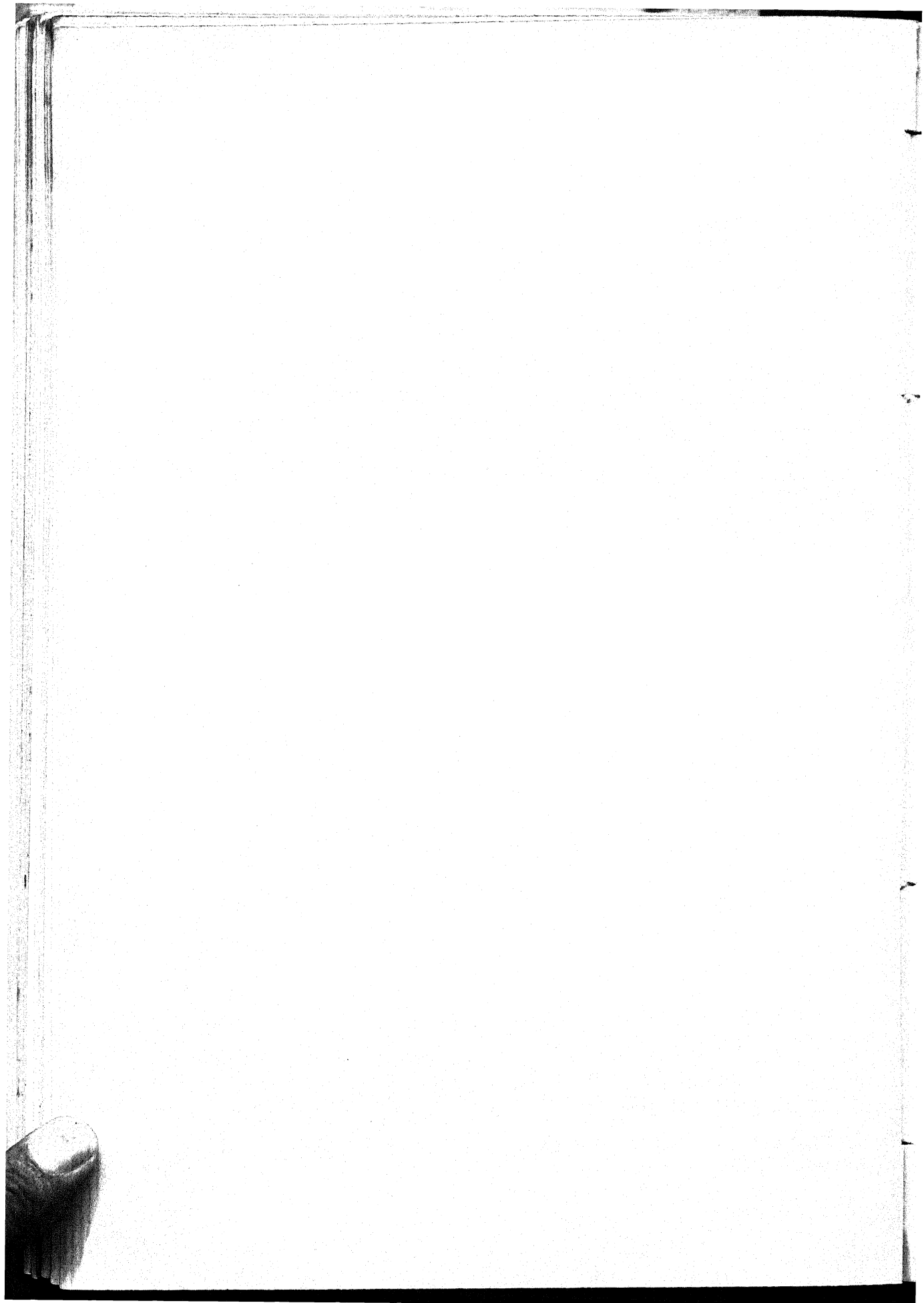
Data were available for only the legumes listed in table 1. Obviously any other legume would have its individual constants which must be determined in the usual manner. Then this technique could be used with any similar set of data. Rather than make nitrogen determinations on a complete set of samples, it is suggested that they be made on replicates of a few selected samples in the low-yielding and in the high-yielding ranges. From these data the regression coefficient and regression equation could be established, from which the amount of nitrogen could be predicted in all other samples from the experiment. This procedure could also be followed when the same legumes are grown during different seasons with varying day lengths.

SUMMARY

A statistical study of 398 samples of leguminous plants showed that total yield was highly correlated with the amount of nitrogen recovered by analysis. By use of the regression equation it is possible to predict, with a high order of precision, the amount of nitrogen in the samples from the dry weight of legumes grown in greenhouse sand cultures.

REFERENCES

- (1) ALLAM, F. 1931 Vom Energieverbrauch der Knöllchenbakterien bei der Bindung des Luftstickstoffs. *Ztschr. Pflanzenernähr. Düngung. u. Bodenk.* (A) 20: 270-301.
- (2) ERDMAN, L. W. 1947 Strain variation and host specificity of *Rhizobium trifolii* on different species of *Trifolium*. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 255-259.
- (3) FIREMAN, M., AND WADLEIGH, C. H. 1951 A statistical study of the relation between pH and the exchangeable-sodium-percentage of Western soils. *Soil Sci.* 71: 273-285.
- (4) GEORGI, C. E. 1935 Influence of the carbohydrate-nitrogen relation on nodule production by red clover. *Jour. Agr. Res.* 51: 597-612.
- (5) SNEDECOR, G. W. 1946 Statistical Methods, ed. 4. The Collegiate Press, Ames, Iowa.
- (6) WILSON, P. W., HOPKINS, E. W., AND FRED, E. B. 1931 Fixation of nitrogen by leguminous plants under bacteriologically controlled conditions. *Soil Sci.* 32: 251-269.
- (7) WILSON, P. W., WENCK, P., AND PETERSON, W. 1933 A statistical study of nitrogen fixation by clover plants. *Soil Sci.* 35: 123-243.



STABILITY OF DDT AND ITS EFFECT ON MICROBIAL ACTIVITIES OF SOIL

L. W. JONES

Utah Agricultural Experiment Station

Received for publication July 23, 1951

New insecticides are being successfully used to control soil-inhabiting forms of life such as wireworms, potato tuber flea beetles, and white grubs. With their increased use the need for studies on their toxicity to soil microorganisms has become more imperative.

Some studies have been made on the toxicity of DDT to soil microorganisms. Appleman and Sears (1) found no unfavorable results on legume nodulation when soil treatments with DDT did not exceed 100 pounds per acre. Payne and Fults (4), however, noted that use of 103 pounds of DDT per acre reduced the number of nodules on bean roots more than half. Wilson and Choudhri (7) found no effects of DDT in concentration of 5 per cent on bacterial numbers or on ammonifying and nitrifying bacteria. No effects on nodulation were noted with DDT in concentrations as high as 2 per cent. Smith and Wenzel (6) observed no definite injury to soil microorganisms from DDT in concentrations up to 400 pounds per acre.

This study was designed to find at what concentrations DDT would be non-toxic to microorganisms and, when added in toxic concentrations, the duration of the injury and the stability of DDT.

EXPERIMENTAL PROCEDURE

Two types of soil were selected: A fertile black loam high in organic matter, and a sandy loam low in organic matter. Samples of each soil type were taken from two different field locations. Each soil was air-dried and passed through a 20-mesh sieve. Soils were weighed out into individual samples, and 50 per cent wettable DDT in concentrations of 1.0, 0.5, 0.25, 0.125, 0.1, 0.01, 0.001, and 0 per cent was added. Each sample was then mixed in a ball mill for 30 minutes.

Enough dry soil was removed to make the nitrification, ammonification, and nitro-fixation determinations. Then 2,500 gm. of each sample was weighed into containers and sufficient water added to bring the soils to 50 per cent of their water-holding capacities. They were then stored in an incubator held constant at 28°C. Water was added weekly to bring the soils up to their original weights. At intervals of analysis, soils were air-dried, ground, and sampled.

Ammonification was determined by incubating, for 7 days at 28°C., three replicate 50-gm. samples containing 1 per cent dried blood and water equal to 50 per cent of their water-holding capacity. Incubated samples were extracted with water acidified with H_2SO_4 to give a pH of about 4.7, and ammonia was distilled from basic solution. When boiled, extracting solutions containing chlorides or acetates were found to introduce an error caused by small quantities of volatile acids distilling over even in basic solutions.

Nitrates were determined in the same manner except that the incubation period

was 21 days and nitrates were reduced to ammonia by Devarda's alloy. Attempts were made to use the perfusion method of Lees and Quastel (3), but fluctuation of water pressure and unequal rates of percolation in the treated and untreated soils made it necessary to discontinue this method.

Methods for plate counts and nitrogen-fixation determinations were those described by Greaves and Jones (2).

DDT was determined by the method of Schechter *et al.* (5). Preliminary studies showed that known quantities of DDT added to soils were completely recovered by extraction with benzene, thus indicating that the method could be used on soil. Duplicate 10-gm. samples were extracted by shaking 10 minutes with 50 ml. benzene. Amounts extracted from incubated samples were compared with control

TABLE 1
Influence of DDT on $\text{NH}_4\text{-N}$ production by soil microorganisms

STORAGE PERIOD	NH ₄ -N RECOVERED FROM SOIL*							
	0 DDT	0.001% DDT	0.01% DDT	0.1% DDT	0.125% DDT	0.25% DDT	0.5% DDT	1.0% DDT
yr.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
0	83.5	95.1	83.5	77.5	73.8	67.5	71.5	69.7
$\frac{1}{2}$	96.8	102.9	99.6	91.7	81.4	71.0	64.3	54.2
1	88.0	89.2	87.0	68.1	54.5	49.0	42.5	30.5
2	73.6	72.0	75.6	69.5	66.1	59.0	53.0	47.6
3	97.8	97.1	92.3	91.8	90.9	82.4	76.6	74.7
Mean.....	87.9	91.3	87.6	79.7	73.3	65.8	61.6	55.3

5 per cent level of significance for concentration means..... 9.4

1 per cent level of significance for concentration means..... 12.7

* Triplicate determinations were made on each of the four soil samples after incubation at 28°C. for 7 days with 1 per cent dried blood. As the trend was much the same for each soil, results were averaged. They are presented on 100-gm. basis.

samples to which equal quantities of DDT had been added and mixed just before analysis. Comparison of results on duplicate incubated samples indicated uniform distribution of insecticide.

Sulfur oxidation was determined by adding 0.25 per cent sulfur to 50 gm. soil weighed in triplicate, water added, and soil incubated for 1 month at 28°C., after which soils were extracted with water acidified with HCl and sulfates determined turbidimetrically by adding BaCl_2 .

RESULTS

In preliminary experiments no inhibition of nonsymbiotic nitrogen fixation by DDT concentrations of 1 per cent was noted either in soil or in solution.

Concentrations of DDT of approximately 0.1 per cent and above had an inhibiting effect on production of ammonia by soil microorganisms (table 1).

In the lower concentrations of 0.001 and 0.01 per cent no evidence of toxicity

to nitrifying bacteria was noted, but at 0.1 per cent and above, definite inhibition of the nitrifiers was evidenced and increased with concentration. After 3 years of

TABLE 2
Influence of DDT on NO₃-N production by soil microorganisms

STORAGE PERIOD	NO ₃ -N RECOVERED FROM SOIL*							
	0 DDT	0.001% DDT	0.01% DDT	0.1% DDT	0.125% DDT	0.25% DDT	0.5% DDT	1.0% DDT
yr.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
0	40.1	40.8	42.9	25.8	19.6	15.4	13.0	9.2
1	41.0	42.5	39.5	29.2	26.1	22.0	12.4	7.1
2	39.2	36.1	39.8	32.8	18.7	13.7	6.4	4.0
3	43.5	41.5	38.5	34.0	35.0	31.0	24.5	20.0
Average.....	41.0	40.2	40.2	30.5	24.9	20.5	14.1	10.1

5 per cent level of significance for concentration means..... 6.13

1 per cent level of significance for concentration means..... 8.35

* Determinations made on soil samples after incubation at 28°C. for 21 days with 1% dried blood and presented on 100-gm. basis.

TABLE 3
Percentage recovery of DDT from four soils after 1, 2, and 3 years of storage

SOIL*	DDT RECOVERED FROM SOIL												
	1st Year Storage				2nd Year Storage				3rd Year Storage				Average
	1% DDT	0.5% DDT	0.25% DDT	0.125% DDT	1% DDT	0.5% DDT	0.25% DDT	0.125% DDT	1% DDT	0.5% DDT	0.25% DDT	0.125% DDT	
	%	%	%	%	%	%	%	%	%	%	%	%	%
1	100	99	90	92	100	90	93	54	85	80	77	50	84.2
2	96	100	100	95	100	100	83	50	96	88	74	53	86.3
3	100	100	97	99	80	57	50	39	73	60	40	40	69.6
4	100	98	91	98	64	54	44	26	55	41	30	19	60.0
Average.....	99	99.3	94.5	96	86	75.3	67.5	42.3	77.2	67.2	55.3	40.5	
Storage mean..	97.2				67.8				60.1				

5 per cent level of significance for concentration means..... 6.49

5 per cent level of significance for storage means..... 2.29

5 per cent level of significance for soil means..... 3.74

* Soils 1 and 2 were sandy and low in organic matter. Soils 3 and 4 were black loams high in organic matter. Soil 4 was a little higher in nitrogen than soil 3.

storage the toxicity of the DDT was not nearly so evident as during the first 2 years (table 2).

During the first year no significant loss of DDT occurred (table 3). During the second year, the loss was appreciable, especially in the fertile soils and in soils

containing low concentrations of insecticides. This loss from storage diminished the third year.

Plate counts were run on all soils at the end of 6 months and 2 years of storage. These indicated that DDT increased the numbers of microorganisms growing on plates. At the end of 6 months on soils containing 0.25 per cent concentration of DDT the count was approximately five times as great as that on untreated soil. At the 1 per cent concentration of DDT the numbers of microorganisms were about double the control. At the end of 2 years the count was still maximum with 0.25 per cent DDT but was back to control levels at a concentration of 1 per cent.

In soils high in organic matter, DDT in concentrations below 0.5 per cent was not toxic to sulfur-oxidizing bacteria but was toxic in 0.1 per cent concentration in the sandy soils. No toxicity was noted at the 0.01 and 0.001 per cent levels.

DISCUSSION

DDT in concentrations of 0.01 and 0.001 per cent was not toxic to nitrifiers, ammonifiers, and sulfur-oxidizing microorganisms of the soil. On the basis of a 2,000,000-pound acre-foot of soil, this amount would represent 200 and 20 pounds of DDT respectively. In concentrations of DDT ordinarily added to soil no evidence of toxicity to any of the important microbial processes was noted. In abnormally high concentrations, however, injury was noted. This injury was still in evidence after 3 years of soil storage under carefully controlled laboratory conditions. Greater injury was noted in soils low in organic matter, and this injury was greater to nitrifiers than to ammonifiers.

Annual analysis of soils indicated DDT to be rather stable the first year, but by the second and third year appreciable amounts of DDT had disappeared, especially in the lower concentrations studied. Although concentrations analyzed were abnormally high, the higher rate of breakdown in the lower concentrations and in the fertile soils suggests the possibility of even more rapid breakdown at concentrations ordinarily added. In view of the favorable temperature and moisture conditions at which these soils were continuously stored and the stability of DDT especially during the first year of storage, this compound showed great stability in the soil and might accumulate in harmful amounts if added yearly in too high concentrations.

There seems to be no correlation between the numbers of microorganisms as determined by the plate count and the injury to specific groups of soil microorganisms such as sulfur-oxidizing, ammonifying, and nitrifying bacteria. Instead of a decrease at higher concentrations, an increase in numbers was noted.

SUMMARY

No injury to nitrifiers, ammonifiers, and sulfur-oxidizing microorganisms was noted from concentrations of DDT ordinarily added to soils. In all cases toxicity began to be manifested at concentrations of about 0.1 per cent.

No injury to the nitrogen-fixing bacteria was observed in soils containing concentrations of DDT as high as 1 per cent.

No injury to the organisms as determined by the plate count was noted. Instead, a stimulation was observed.

DDT added to the soil was remarkably stable during the first year of storage but by the end of the second and third years appreciable breakdown had occurred. The breakdown was greater in soils containing the lowest concentrations of DDT and also in soils high in organic matter.

REFERENCES

- (1) APPLEMAN, M. D., AND SEARS, O. H. 1946 Effect of DDT on nodulation of legumes. *Jour. Amer. Soc. Agron.* 38: 545-550.
- (2) GREAVES, J. E., AND JONES, L. W. 1941 Survival of microorganisms in alkali soils. *Soil Sci.* 52: 359-364.
- (3) LEES, H., AND QUASTEL, J. H. 1946 Soil nitrification. *Biochem. Jour.* 40: 803-828.
- (4) PAYNE, M. G., AND FULTS, J. L. 1947 Some effects of 2,4-D and Colorado 9 on root nodule in the common bean. *Jour. Amer. Soc. Agron.* 39: 52-53.
- (5) SCHECHTER, M. S., et al. 1945 Colorimetric determination of DDT. *Indus. and Engin. Chem., Analyt. Ed.* 17: 704-709.
- (6) SMITH, N. R., AND WENZEL, M. E. 1948 Soil microorganisms are affected by some of the new insecticides. *Soil Sci. Soc. Amer. Proc.* (1947) 12: 227-233.
- (7) WILSON, J. K., AND CHOUDHRI, R. S. 1946 Effects of DDT on certain microbiological processes in the soil. *Jour. Econ. Ent.* 39: 537-538.

COLLECTION AND PRESERVATION OF SOIL PROFILES: II¹

HENRY W. SMITH, R. A. MCCREERY, AND C. D. MOODIE

Washington Agricultural Experiment Stations

Received for publication August 3, 1951

A continuing interest in the preparation of soil monoliths by the procedure of Smith and Moodie (5) is evident from the notes concerning it which have appeared since 1947 (1, 3, 4, 6). Some of the suggestions contained in these papers, together with changes of techniques developed here, seem worthy of unified presentation. Further, since the original article paid scant attention to the details of procedure after the profile was glued to the mounting board, those aspects require elaboration.

MODIFICATIONS OF FIELD PROCEDURE

The essential features of the method described in 1947 (5) are retained, but one important change has been made. This is the substitution of vinylite resin solution for dilute cellulose acetate as the initial spray. This represents a further adoption of the techniques of Berger and Muckenhirn (2). An 8 per cent solution, because it is more easily handled in the spray pump,² is still preferred over the 12 per cent concentration. Use of vinylite is particularly recommended for the sampling of very sandy or gravelly soils of any moisture content, and for dry silty nonaggregated soils that are wetted with difficulty. Waiting times previously specified following spraying are now employed but rarely. Five minutes for the spray to dry is sufficient for all save an occasional soil with completely incoherent layers. For those few, it is wise to wait for several hours, rather than for 30 minutes only.

Lyford³ and later Berger and Muckenhirn used cheesecloth strips to give stability to incoherent soils; these strips are equally useful to speed the field process in sampling any soil. After the concentrated cellulose acetate is applied, a folded strip of coarsely woven cloth, slightly narrower than the soil section to be sampled, is laid against the freshly applied cellulose acetate, sprayed lightly with vinylite resin, and pressed into the still-fluid acetate. Within 2 or 3 minutes a protective board can be laid against the profile strip, and excavation started. This revised procedure speeds up the field process at least as well as the box technique of Bentley and Odynsky (1). Although the method recently suggested by them has been employed on occasion in Washington since 1945, it is not recommended for general use.

¹ Scientific Paper No. 1051, Washington Agricultural Experiment Stations, Institute of Agricultural Sciences, The State College of Washington, Pullman.

² Most successful of the pumps employed is the chemical sprayer manufactured by the Dobbins' Manufacturing Company, at Elkhart, Indiana. It is helpful to coarsen the spray by reaming out the nozzle very slightly with a drill. The resin solution can be left in the sprayer for months without clogging. Other pumps have developed a variety of defects.

³ Typed copy, dated September, 1940, supplied by W. H. Lyford, Jr., University of New Hampshire, Durham.

The only soils that have not been found amenable to the usual procedure are peats and mucks. For sampling these, a small pit (dimensions no more than 2 by 3 feet are required) is dug to the desired depth. One face of the excavation is smoothed with a sharp, flat spade, or preferably a lawn-edging tool. A section at least one third again as wide as that required for the final monolith is marked out,

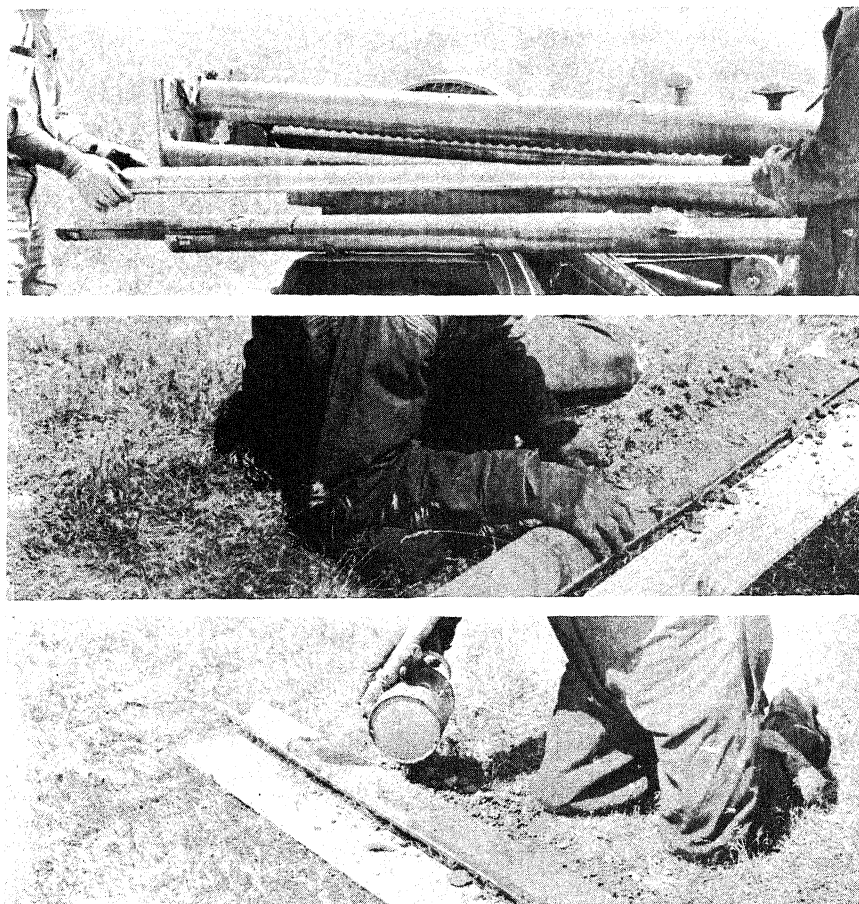


FIG. 1. TOP, THE EAVES-TROUGH IS LOWERED ON THE CORE IN THE SPLIT BRASS TUBE. CENTER, THE CORE IS SPLIT ALMOST TO THE CENTER. BOTTOM, THE SOIL SURFACE IS SATURATED WITH VINYLITE RESIN.

and the lawn-edging tool is used to cut down the lines to the bottom of the pit. A 3- or 4-inch depth of cut is sufficient. A rough board is then held against the face of the vertical section while the tool is pushed down to sever the soil from the pit wall. Sometimes an occasional cloth tie around the soil and board, at the top, is needed. A little prying and lifting will bring the peat or muck section to the surface. It can then be wrapped for transport on this same board. The entire process takes no more than 10 minutes as a rule. After several weeks the material

will have dried and shrunk to stable dimensions; during this drying process it is wise to push the drying pieces together to maintain a natural appearance. The profile can then be transferred to the final board, trimmed, glued, and prepared in the usual manner.

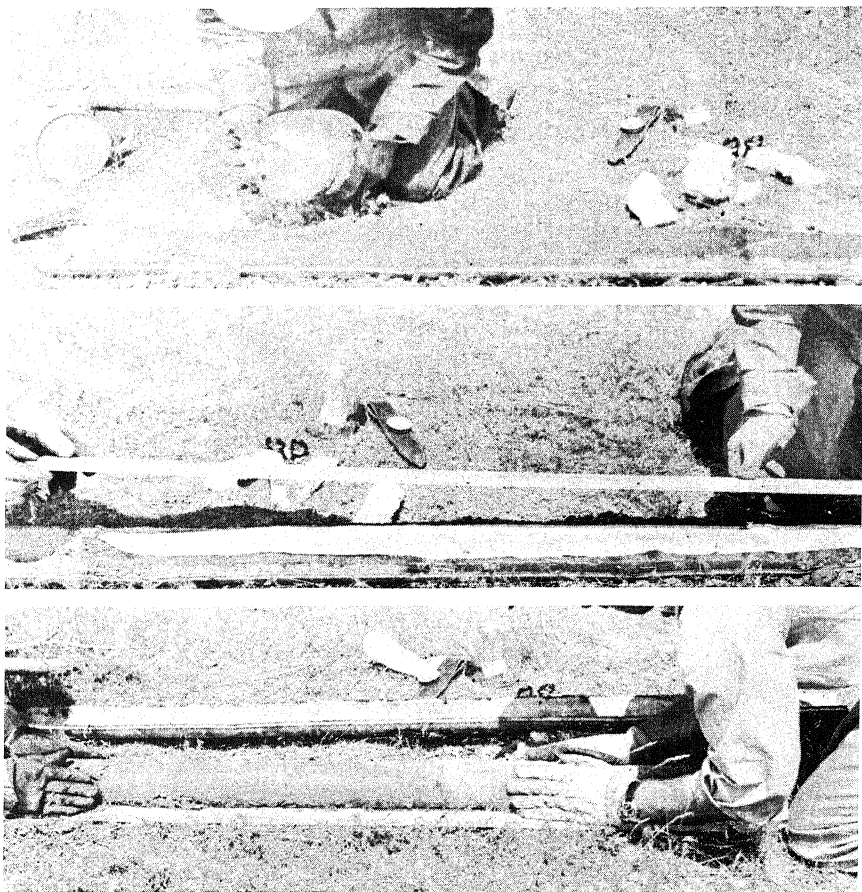


FIG. 2. TOP, CONCENTRATED CELLULOSE ACETATE IS APPLIED IN A BAND. CENTER, THE MOUNTING BOARD IS PLACED ON THE SPLIT CORE, TO WHICH HAS BEEN ADDED A STRIP OF CLOTH AND ADDITIONAL CELLULOSE ACETATE. BOTTOM, THE SYSTEM HAS BEEN TURNED OVER, AND THE PROFILE IS STRAIGHTENED ON THE BOARD.

USE OF THE KELLEY CORE SAMPLER

Recently a core-sampling machine⁴ has been used for collecting monolith samples. The procedure of Matelski has been altered in some of its details (figs. 1 and 2). The core is rolled into a section of metal eaves-trough, split longitudinally not quite to the center, and then sprayed with 8 per cent vinylite resin. Within 2 or 3 minutes a thin strip of cellulose acetate is poured on the soil surface. Commonly

⁴ Made available to us through the courtesy of O. J. Kelley.

a narrow folded length of coarsely woven cheesecloth is then spread on the profile, and another strip of cellulose acetate is added. No brushing of the cellulose acetate is required. The mounting board is then laid on top, and the entire system turned over. The eaves-trough can then be lifted off, and the profile wrapped with sacking for transport. Use of the cheesecloth will prevent the soil core from sliding on the board, even though it is transported over rough roads long before the

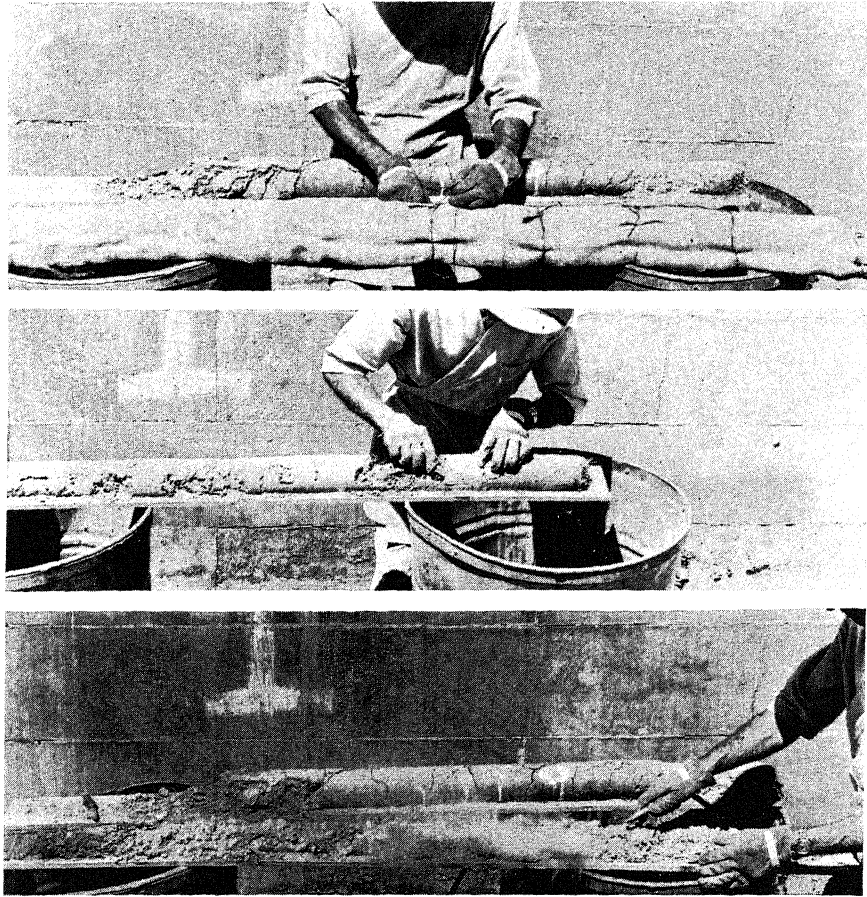


FIG. 3. TOP, PROFILES FROM THE FIELD ARE UNWRAPPED. CENTER, A KNIFE IS USED TO LOOSEN STRUCTURAL UNITS. BOTTOM, AN AIR STREAM LOOSENS AND REMOVES EXCESS SOIL.

cellulose acetate has dried. With a crew of three, it is not difficult to complete the entire operation of sampling to 6 feet, preparing the monolith, and readying the machine for travel to the next site in as little as 20 minutes.

REMOVAL OF EXCESS SOIL

Illustrated in figures 3 and 4 is the present procedure for removal of excess soil. By using an air jet and prying carefully with a knife, it is possible to expose un-

marred structural units in most soils. If the soils are worked out within a few days of the sampling date, results will usually be more satisfactory. Massive structures are particularly difficult to handle when the soil has dried completely. It is feasible to wet a completely dry soil and work it out after the moisture has reached an equilibrium state, but the usual technician may not always bother to do so. The vacuum cleaner technique of Bentley and Odynsky is occasionally

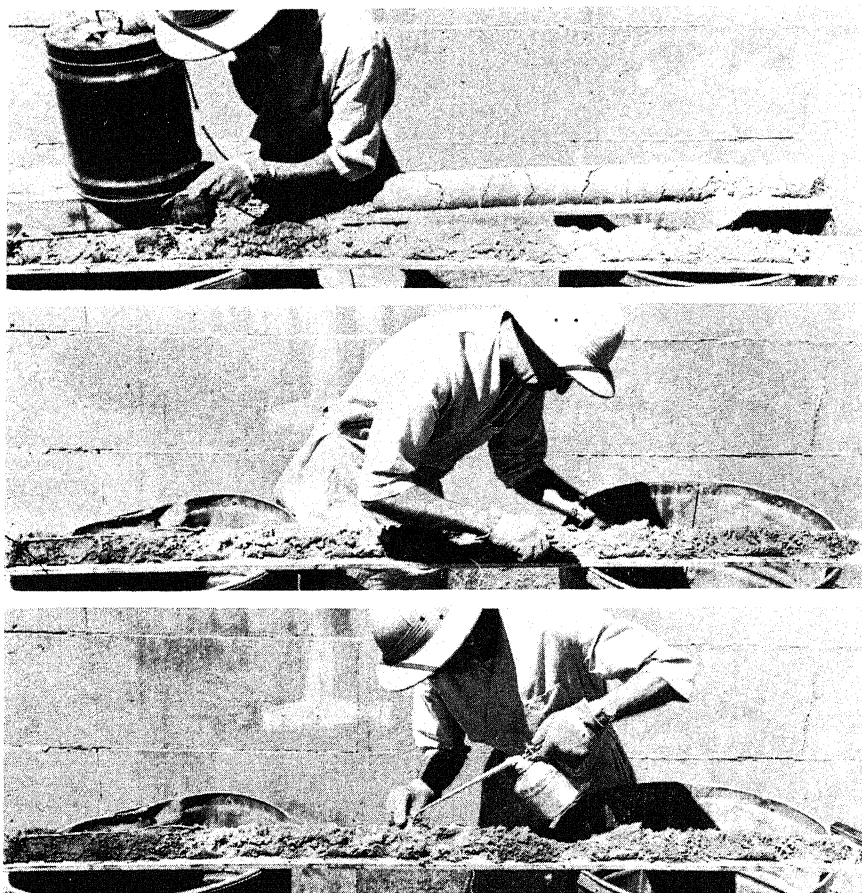


FIG. 4. TOP, VINYLITE RESIN IS ADDED SLOWLY TO SATURATE SUCCESSIVE SMALL PORTIONS OF THE PROFILE. CENTER, THE EDGES OF THE BOARD ARE CLEANED WITH A WOOD SCRAPER. BOTTOM, LOOSE UNITS ARE GLUED WITH CELLULOSE ACETATE.

useful but has not replaced use of an air jet in this laboratory. Whatever the technique, particular care should be used to remove all extraneous material, but the board should not be tipped at this stage. It is not necessary that all soil material be firmly fixed, since pouring with vinylite resin will effect that.

FINISHING THE PROFILE

The spraying technique of Smith and Moodie is unsatisfactory for many soils. The soil material is insufficiently fixed, and in some of the dry silty brown and

sierozem soils of central Washington the resin is absorbed by only a thin surface layer. The pouring technique of Berger and Muckenhirn has been used; it is better but not ideal. Recently the more satisfactory method illustrated in figure 4 has been used. If the rate of flow of 8 per cent resin through the siphoning tube is kept low, the entire profile can be completely saturated with no need for pieces of board clamped on the side as was suggested by Berger and Muckenhirn. There is no waste of resin and almost no tendency for a surface film of resin to form on the soil, particularly if the 8 per cent concentration is used. The technique has been highly satisfactory for a variety of soils.

Following the resin treatment, there will often be loose soil pieces or sections of profile. Concentrated cellulose acetate is often required to fix them permanently. To pour concentrated cellulose acetate down a small crack is difficult; lifting a large soil piece, applying glue, and then replacing the section often result in destruction of the natural appearance of the profile. A pump-type oil can, to dispense the concentrated cellulose acetate, is useful. If the can is kept full and a tightly fitting rubber cap is placed on the spout, no difficulty with clogging has been encountered, even with lapses of several months between use. It is *not* satisfactory to clean the pump each time with a solvent, since the valve then commonly fails to work when the can is refilled for use. Cellulose acetate so dispensed is particularly useful when a peat or muck soil is being stabilized.

SHIPPING OF PROFILES

Although crating for shipping requires considerable care, sending the samples by freight or express is entirely feasible. The profile should be wrapped and taped, and then cushioned with ample packing material. A rigid type of packing must be avoided; otherwise soil pieces will be loosened from the board as a result of rough handling.

REFERENCES

- (1) BENTLEY, C. F., AND ODYNSKY, W. 1949 Minimizing the field time required for preparing permanent soil profiles. *Agron. Jour.* 41: 99-100.
- (2) BERGER, K. C., AND MUCKENHIRN, R. J. 1946 Soil profiles of natural appearance mounted with vinylite resin. *Soil Sci. Soc. Amer. Proc.* (1945) 10: 368-370.
- (3) LYND, J. Q. 1950 Soil monolith displays. *Agron. Jour.* 42: 574-575.
- (4) MATELSKI, R. P. 1949 Use of the Kelley soil sampling machine in Nebraska. *Agron. Jour.* 41: 394.
- (5) SMITH, H. W., AND MOODIE, C. D. 1947 Collection and preservation of soil profiles. *Soil Sci.* 64: 61-69.
- (6) WOODS, JACK E. 1950 Plant monoliths . . . A new visual aid. *What's New in Crops and Soils* 3: 16-22.

BOOKS

Bacterial Physiology. Edited by C. H. WERKMAN AND P. W. WILSON. Academic Press, Inc., New York, 1951. Pp. 707. Price \$8.50.

The 19 contributors to this volume have endeavored to present modern concepts on the chemistry and structure of bacterial cells, inheritance, variation, adaptation, and growth of bacteria, physical and chemical factors affecting growth and death, bacterial enzymes, anaerobic dissimilation of carbohydrates, bacterial oxidations, autotrophic and heterotrophic assimilation of carbon dioxide, organic nitrogen, biological nitrogen fixation, mineral metabolism, biochemistry of molecular hydrogen, assimilation by bacteria, degradation and synthesis of complex carbohydrates, significance of autotrophy, and luminous bacteria. No attempt was made to assemble extended bibliographies, but a list of about 1900 titles is appended to the volume. The primary purpose has been to develop a comprehensive text for graduate students in bacteriology and biochemistry. The volume will be highly useful for reference by those engaged in soil-plant research.

The Chemistry and Technology of Food and Its Products. Volume 3, Revised. Edited by MORRIS M. JACOBS. Interscience Publishers, New York, 1951. Pp. 808. Price \$15.

This, the final volume of a set comprising 2,580 pages, contains a complete outline of the contents of all three volumes and the combined index as well. The 22 contributors to volume 3 have prepared comprehensive, up-to-date reviews on methods of food preservation, including dehydration, temperature control, use of hermetically sealed containers, microorganisms, and chemical preservatives, and packaging. Similarly, they have dealt with methods of food production, with special reference to cereal grains, bread, sugars, confections, chewing gum, fruit juices, milk, meat, fish, fats, beverages, and industrial waters. One chapter outlines the uses to which enzymes are put in food processing. The volume is well illustrated, containing a large number of photographs, flow sheets, diagrams, and other types of figures. Each chapter is well documented with references at the bottoms of the pages. The index covers nearly 77 pages. The set as a whole represents a prodigious amount of work on the part of the authors and the editor, who are to be congratulated on having brought this enterprise to such a successful conclusion.

Field Crops. Second Edition. By HOWARD C. RATHER AND CARTER M. HARRISON. McGraw-Hill Book Company, Inc., New York, 1951. Pp. 446, figs. 129. Price \$5.50.

The 23 chapters in this book deal with the problems involved in soil preparation for farm crops and in their seeding, growing, and harvesting. It is designed for use in a beginning course in agricultural colleges and for reference purposes for classes in vocational agriculture. Rapid developments in the science and prac-

tice of crop production make it necessary to revise such texts fairly frequently. The second edition of this book meets the requirements admirably. The material is well presented, the illustrations are excellent, and the student will get a good up-to-date view of the subject.

Mineral Nutrition of Plants. Edited by EMIL TRUOG. The University of Wisconsin Press, Madison, 1951. Pp. 469. Price \$6.

This volume contains 18 papers written by 22 soil-plant scientists and presented at a symposium in celebration of the 100th anniversary of the founding of the University of Wisconsin. The subjects covered include world food possibilities, soil as a medium for plant growth, activities of soil-colloid cations, availability of soil anions, contact phenomena, soil physical properties, soil micro-organisms and nutrient availability, solute accumulation in roots, mechanism of ion absorption, translocation of minerals, control of nitrogen effects in apples, vegetable production, criteria in determining essential nature of nutrients, mineral nutrition and plant ontogeny, protein-carbohydrate metabolism, light as a modifying influence, soil moisture and mineral nutrition, and environmental influences on growth of sugar cane. The authors are Arnon, Biddulph, Bodman, Boynton, Broyer, Burström, Clements, Dean, Hester, Jenny, Kellogg, Lochwing, Marshall, Norman, Orvedal, Overstreet, Page, Richards, Steinberg, Truog, Wadleigh, and Withrow. This is a highly valuable collection of papers of sufficient variety to be of interest to all workers in soil and plant research.

THE EDITORS

PLAN CONFERENCE ON CLAYS

A conference on clays will be held on the Berkeley campus of the University of California, July 21 to 25. The program will cover structure, properties, and methods of identifying clays. Speakers are being invited from among those interested in soil science, ceramics, petroleum engineering, civil engineering, and other related fields of research. The National Clay Mineral Committee, which was organized at the meeting of the American Institute of Mining and Metallurgical Engineers in St. Louis in 1951, will hold a session during the conference, under the chairmanship of R. E. Grim, to consider the establishment of an organization of persons interested in clay mineralogy.

The conference steering committee is composed of George S. Gates, U. S. Bureau of Mines; J. Schlocker, U. S. Geological Survey; M. D. Turner, California State Division of Mines; and I. Barshad, H. E. Davis, C. M. Gilbert, I. Goldberg, W. P. Kelley, A. Klein, A. Pabst, W. H. Somerton, and J. A. Pask, Chairman, University of California.

A CONCEPT CONCERNING THE MEASUREMENT OF AVAILABLE SOIL NUTRIENTS

MAURICE FRIED AND L. A. DEAN¹

U. S. Department of Agriculture

Received for publication August 14, 1951

BASIC PRINCIPLES

The availability of a nutrient element in the soil is determined by the various factors that affect absorption of the element by plants. The amount of the nutrient available in a soil depends not only upon the soil itself but also upon the specific conditions under which a given crop is grown. In a true sense, the plant is the only agent that can determine the amount available.

Measurement of the amounts available implies that a comparison with an accepted standard has been made. The concept presented in this paper provides a basis by which a given nutrient in a soil is compared to that of a standard containing this nutrient. It is assumed that the definition of "available nutrient in the soil" implies that when two sources of a given nutrient are present in the soil the plant will absorb from each of these sources in proportion to the respective quantities available.

Let us assume a soil with two sources (*A* and *B*) of a nutrient (phosphorus for example). If the plants growing in this soil absorb nutrient from the two sources in direct proportion to the respective amount available then:

$$\frac{A_{\text{soil}}}{B_{\text{soil}}} = \frac{A_{\text{plant}}}{B_{\text{plant}}} \quad (1)$$

where A_{soil} and B_{soil} represent the amounts of available nutrient in sources *A* and *B*, and A_{plant} and B_{plant} are the amounts of nutrients the plants have absorbed from sources *A* and *B*.

Equation (1) provides a basis by which the available nutrient in a soil can be compared with that of a standard and its amount measured. Let source *A* be the supply of a nutrient in the soil, and source *B*, the standard that has been introduced into the soil for comparison. This standard is a chemical compound containing the nutrient under consideration.

If *A* and *B* are the only two sources of the nutrient for the plant, the total amount absorbed equals $A_{\text{plant}} + B_{\text{plant}}$. Thus, let $y = \frac{B_{\text{plant}}}{A_{\text{plant}} + B_{\text{plant}}} =$ proportion of the nutrient in the plant derived from the standard; $A = A_{\text{soil}} =$ amount of nutrient available in the soil; $B = B_{\text{soil}} =$ amount of nutrient added

¹ This investigation was supported in part by the U. S. Atomic Energy Commission. The authors express their appreciation to W. K. Robertson and J. M. Blume for making available the unpublished data in table 6 and to D. D. Mason for suggestions regarding the statistical analyses.

as the standard. Solving for B_{plant} in terms of y , and substituting in equation (1),

$$A = \frac{B(1 - y)}{y} \quad (2)$$

Accordingly, the amount of available nutrient in the soil, A , can be measured if y , the proportion of nutrient in the plants derived from the standard can be determined.

In short, the proposed method for measuring the amount of available nutrient in soils involves the introduction of a known quantity of a standard source of the nutrient under consideration into a soil, growing the desired crops, determining the proportion of the total nutrient absorbed that was derived from the standard source, and calculating the amount of available nutrient in the soil, A , by use of equation (2). This measured quantity has the same dimensions as the standard. For example, if monocalcium phosphate was the standard and phosphorus was the nutrient under consideration, A would be in terms of the added monocalcium phosphate.

The basis suggested for measuring the amount of an available nutrient in soils presumes a particular behavior pattern by plants in respect to nutrient availability and absorption. Thus there remains the necessity of setting up suitable methods of experiment to meet the restrictions imposed. The two sources of nutrient under consideration, namely, the soil and the standard, must be equally accessible to the plant. Satisfactory techniques are needed for determining y , the proportion of the nutrient in the plant derived from the standard. This latter may best be accomplished through use of radioactive or stable isotopes.

The interpretation of the A values calculated from experimental data is discussed in the succeeding section. In considering these values one should bear in mind that the amount of available nutrient associated with a source is generally somewhat less than would be indicated by its total analysis. The relationship to the amount available may be represented as $A = k C_A$, where C_A is the amount of nutrient in source A , and k is an availability coefficient.

The expression A carries the implication that only a single source of a soil nutrient is being considered. In the case of soil phosphorus it is quite generally recognized that the same soil may contain more than one form of phosphorus available to plants. In such an instance A is considered as a summation as follows:

$$A = kC_A = \Sigma(k_1C_{A_1} + k_2C_{A_2} + \dots + k_nC_{A_n}) \quad (3)$$

In other words, each form of a nutrient will have a coefficient of availability peculiar to it and the environmental condition.

APPLICATIONS

The application of the proposed concept to the problem of measuring the amount of available nutrient in soil is presented by discussing several experiments from both greenhouse and field. In each instance it is necessary to determine

whether the methods used provide data to which the concept may be applied and whether departures from the restrictions imposed seriously limit its use.

Experiment I

An experiment was conducted in the greenhouse to measure available phosphorus in soils with monocalcium phosphate containing P32 as a standard. Three soils were selected: Davidson clay loam very low in available phosphorus and two Caribou silt loam soils, one with a medium phosphorus level and the other with a very high phosphorus level. Six rates, from 5.0 to 160 pounds of P_2O_5 per acre were applied by two methods: a mixed and a band placement. In the mixed treatment the monocalcium phosphate was mixed throughout the soil contained in the pots. For the band placement it was placed in a narrow band across the

TABLE 1

Dry weights of oat tops as affected by rate and placement of monocalcium phosphate

TREATMENT P_2O_5 /Acre	YIELD OF OAT TOPS PER POT					
	Davidson soil		Caribou soil 1		Caribou soil 2	
	Mixed placement	Band placement	Mixed placement	Band placement	Mixed placement	Band placement
<i>lb.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
0	1.6	2.1	4.6	4.7	5.2	5.3
5	1.7	2.4	4.5	4.8	5.4	5.5
10	2.0	2.6	4.6	4.8	5.4	5.5
20	2.0	2.7	4.7	4.8	5.6	5.0
40	2.6	3.1	4.9	4.8	5.5	5.6
80	3.0	3.7	5.0	4.9	5.0	5.5
160	3.3	4.1	4.7	5.0	5.9	5.8

L.S.D. (0.05) = 0.62; L.S.D. (0.01) = 0.82.

center of the pot 2 inches below the surface of the soil. Oats were seeded in two parallel rows, $\frac{1}{2}$ inch deep and 1 inch to either side of the fertilizer band. The oat plants were harvested 1 month after emergence, and the dry weights and y , the proportion of phosphorus in the crop derived from the fertilizer, determined.

The yields (table 1) show a definite response to phosphorus in the Davidson soil and an advantage favoring the band placement. In the two Caribou soils treatment failed to affect yield.

The amount of available soil phosphorus, A , was calculated from equation (2). The values obtained from the various treatments are given in table 2. Consider first the results for the mixed placement. One of the basic assumptions is that nutrient absorption from two sources, the soil and a standard, is being compared. It follows, therefore, that values of A obtained should not be affected by the rate of application of the standard. The data obtained for the mixed placement show but little effect of a 32-fold change in rate of application on the calculated A values.

As contrasted with the mixed treatment, lower A values were obtained by

TABLE 2
Influence of rate of application and placement on A values when monocalcium phosphate is the standard and oats the test crop

TREATMENT P ₂ O ₅ /ACRE	AMOUNT OF SOIL PHOSPHORUS A, P ₂ O ₅ /ACRE		
	Davidson soil	Caribou soil 1	Caribou soil 2
<i>Mixed placement</i>			
lb.	lb.	lb.	lb.
5	85	433	1120
10	81	473	1420
20	86	476	1530
40	99	521	1500
80	104	541	1310
160	116	495	1530
L.S.D. (.05)	27	90	263
L.S.D. (.01)	38	128	381
<i>band placement</i>			
5	25	169	621
10	21	194	725
20	23	183	925
40	38	236	871
80	37	259	1180
160	54	365	1450
L.S.D. (.05)	8.0	76	268
L.S.D. (.01)	11.0	107	381

TABLE 3
Influence of rate and placement of monocalcium phosphate on its utilization by oats

TREATMENT P ₂ O ₅ /ACRE	PERCENTAGE UTILIZATION OF FERTILIZER		
	Davidson soil	Caribou soil 1	Caribou soil 2
<i>Mixed placement</i>			
lb.			
5	3.0	3.0	3.3
10	3.3	3.2	2.7
20	2.9	3.2	2.4
40	2.8	3.0	2.3
80	2.6	3.1	2.4
160	2.0	2.9	2.4
<i>Band placement</i>			
5	10.7	9.0	5.7
10	11.3	8.7	5.0
20	8.4	8.1	3.8
40	5.8	6.4	4.0
80	5.4	5.4	2.9
160	4.1	3.7	2.5

L.S.D. (.05) = 0.85; L.S.D. (.01) = 1.12.

using a band placement. Since it probably can be assumed that the method of placement does not change the soil phosphorus, the lower *A* values obtained with the band placement can be attributed to a higher availability of the standard. Reduced phosphate fixation and a higher phosphate concentration at the root surfaces may be contributing factors.

With the band placement and particularly at the high rates of application, the *A* values increase significantly with increasing rates. This suggests that the accessibility to plants of phosphorus added in the band does not remain constant with increasing rates of application. In this connection it is of interest to consider percentage utilization of the fertilizer as affected by placement and rate of application. Such data are given in table 3. Here it is shown that the percentage of the fertilizer application that is recovered by the harvested plants is independent of the rate of application for the mixed application but decreases with the rate of application for the band placement. At all rates studied, but especially at low rates, the efficiency of the band application exceeds that of the mixed.

Experiment II

Another greenhouse experiment, the results of which were reported previously,² compared superphosphate and rock phosphate. The three soils used were selected from an experimental field at Joliet, Illinois. Alfalfa was grown as the indicator crop, and observations were made on four successive cuttings. The superphosphate was applied at the rate of 150 pounds P_2O_5 per acre and the rock phosphate at 700 pounds P_2O_5 . The *A* values calculated from the results of this experiment are given in table 4.

Laboratory and greenhouse experiments have shown that when soluble phosphatic fertilizers are mixed with soil there is a rapid initial fixation of phosphorus followed by a slower transition over an extended period.³ Thus it might be expected that the *A* value calculated for the different cuttings would progressively increase. The data for superphosphate given in table 4 tend to support this contention; however, the marked differences in the *A* values for the third and fourth cuttings are rather surprising. Obviously in this experiment the calculated *A* values for the various cuttings are in terms of soil phosphorus equivalent to the phosphorus of superphosphate which has been in contact with the soil for varying periods.

When rock phosphate rather than superphosphate was considered as the standard, the *A* values were higher for all soils. From what is known of the availabilities of the two materials, this was to be expected. There appears to be no significant change for the various cuttings from the same soil. This possibly indicates little change in the availability of the rock phosphate standard due to

² Fried, M., and MacKenzie, A. J. Rock phosphate studies with neutron irradiated rock phosphate. *Soil Sci. Soc. Amer. Proc.*, (1949) 14: 226-231, 1950.

³ Kurtz, T., DeTurk, E. E., and Bray, R. H. Phosphate adsorption by Illinois soils. *Soil Sci.* 61: 111-124, 1946.

Scarseth, G. D., and Tidmore, J. W. Fixation of phosphates by clay soils. *Jour. Amer. Soc. Agron.* 26: 152-162, 1934.

phosphorus fixation. With rock phosphate, A values for the three soils were quite different. These differences probably reflect the influence of the soil acidity on availability of the rock phosphate.

TABLE 4

*Influence of soil pH and cutting of alfalfa on A value when superphosphate and rock phosphate are used as standards**

SOIL HISTORY	SOIL pH	TIME OF CUTTING	AMOUNT OF SOIL PHOSPHORUS A, P_2O_5 /ACRE MEASURED WITH	
			Superphosphate	Rock phosphate
		<i>weeks</i>	<i>log. lb.</i>	<i>log. lb.</i>
Residues	4.9	8	1.899	2.269
		13	1.901	2.198
		18	1.994	2.185
		23	2.158	2.306
Residues + lime	5.5	8	1.776	2.615
		13	1.837	2.549
		18	1.949	2.516
		23	2.112	2.579
Manure + lime	5.8	8	1.874	2.952
		13	1.952	2.906
		18	2.021	2.849
		23	2.215	2.875

L.S.D. (.05) = 0.0518; L.S.D. (.01) = 0.0713.

* Experience has shown that when A values vary over a fairly wide range there is a positive correlation of the mean and its standard error; therefore, a log transformation was used for the statistical analyses. The log values are retained in this table to enable a direct comparison with the calculated L.S.D.

TABLE 5

*Effect of crop and stage of growth on A virus values when superphosphate is applied in bands**

CROP	AMOUNT OF SOIL PHOSPHORUS A, P_2O_5 /ACRE		
	First sampling	Second sampling	Third sampling
	<i>lb.</i>	<i>lb.</i>	<i>lb.</i>
Cotton.....	95.4	122.0	178
Corn.....	45.0	230.0	410
Tobacco.....	41.2	67.3	132

* Adapted from Nelson *et al.*⁴

Experiment III

A field experiment comparing the phosphorus utilization by cotton, corn, and tobacco was conducted in North Carolina.⁴ Superphosphate labeled with P32 was applied in bands $2\frac{1}{2}$ inches to each side of the seed or plants at the time of planting. The crops were sampled at three stages of growth and the relative

⁴ Nelson, W. L., *et al.* Application of radioactive tracer technique to studies of phosphatic fertilizer utilization by crops: II. *Soil Sci. Soc. Amer. Proc.* (1947) 12: 113-118, 1948.

proportions of soil and fertilizer phosphorus in these samples determined. From the data obtained it was possible to calculate the *A* values given in table 5. These increase with age of the plants. Furthermore, there is a marked difference between the values for corn and the other two crops. Although phosphate fixation may have contributed to the differences with age, other factors must be considered. As the plants grew, the volume of soil phosphorus in range of the roots increased greatly, while the volume of fertilizer phosphorus remained relatively constant. This should lower the proportion of fertilizer to soil phosphorus absorbed, thus giving an increased *A* value. If it can be assumed that the distribution of soil phosphorus within the root zone is relatively uniform, it would follow that the *A* values would reflect the relative size of root systems of the crops. Thus, if field experiments such as this are used to evaluate the available phosphorus of soils, factors affecting root growth may influence the results.

TABLE 6

Effect of rate of application and amount of soil calcium on the determination of A values for calcium

TREATMENT GYPSUM/ACRE	AMOUNT OF SOIL CALCIUM <i>A</i> PER ACRE		
	Low-calcium soil	Medium-calcium soil	High-calcium soil
<i>lb.</i>	<i>lb.</i>	<i>lb.</i>	<i>lb.</i>
75	864	1209	2467
150	972	1151	2415
300	901	1173	2491
600	981	1194	2661
Average.....	930	1182	2509
Coefficient of Variation, %.....	4.2	2.2	3.7
Exchange Ca.....	784	1123	2144
Exchange Ca	1.19	1.05	1.17
<i>A</i> value Ca.....			

Experiment IV

All of the experiments described thus far have dealt with the measurement of soil phosphorus. The movement of phosphate ions in soil is highly restricted, and the two sources of phosphorus—the soil and the standard—can be envisioned as essentially independent. It was, therefore, of interest to examine an experiment involving a nutrient having a less restricted movement, calcium, for example. In this instance the soil calcium and that introduced as a standard will tend to intermingle and there will be an indefinite boundary between soil and standard.

A greenhouse experiment was conducted in which Ca45 labeled gypsum was used as a standard to measure the available calcium in soils. Three soils were selected from a lime experiment at the Maryland Agricultural Experiment Station. Gypsum synthesized to contain Ca45 was mixed at four rates throughout the soil in the pots. The test crop was oats. The *A* values calculated from the results of this experiment are given in table 6.

The A values obtained from this experiment are independent of the rate at which the standard was applied. There is a definite tendency for the values to be slightly higher than the amount of exchangeable calcium determined by extracting soil with ammonium acetate. Possibly this difference is within the limits of the experimental errors involved. When a calcium salt such as gypsum is mixed with neutral and acid nonsaline soils, it is probable that this calcium rapidly becomes indistinguishable from the exchangeable calcium native to the soil. Thus, if the exchangeable calcium is the only form of calcium in the soil available for absorption by plants the A value should equal the exchangeable calcium determined by laboratory procedures.

DISCUSSION

The proposed concept for measuring soil nutrients is similar in principle to the well-known technique for analysis by isotope dilution methods.⁵ In general, these methods embrace addition of an isotopically labeled compound to an unknown mixture followed by isolation of the same compound from the system. The specific activity of the original compound is then compared with the isolated sample. Equation (2) can be used to calculate the amount of compound in the unknown mixture.

If the soil is considered as the unknown mixture and the plant the isolation method, the similarity between this proposal for measuring the available soil nutrients and the dilution methods is apparent. One difference is the nature of the intermingling of standard and unknown required. For example, when a P32 labeled phosphate compound is added to a soil the amount by which the available soil phosphorus is diluted is measured by the ratio of the specific activity of the phosphorus in the plants grown to that of the added phosphate. In this instance the isotopic dilution may take place within the plants rather than in the soil. A mathematical expression similar to equation (2) was noted by Larsen⁶ in discussing the results from a tracer experiment on the uptake of soil and fertilizer phosphorus by plants. In this instance it was presumed that the isotopic dilution took place in the soil.

The experiments described in the foregoing section have shown that factors such as phosphate fixation, character of the standard compound, soil acidity, and method of placement may affect the degree to which the available soil phosphorus is diluted. This does not appear to invalidate the A values calculated but does impose restrictions on their interpretation. On the other hand, it provides a basis for evaluation of factors affecting nutrient availability.

In the use of the suggested method for determining soil nutrients the choice of a standard will largely govern the interpretations that can be placed upon the results obtained. Additional investigation will be necessary before the most satisfactory standards for specific purposes are developed.

⁵ Kamen, M. D. *Radioactive Tracers in Biology*, pp. 112-118. Academic Press, Inc., New York, 1947.

⁶ Larsen, S. *Studies on the uptake of phosphorus in plants with radiophosphorus as an indicator*. K. Veterinaer- og Landbohøjskole, Copenhagen, Denmark, (Mimeographed). 1950.

SUMMARY

The concept that a plant having two sources of a nutrient will absorb its nutrients from each of these sources in direct proportion to the amounts available has the following logical consequence: The quantity of available nutrient in the soil can be determined in terms of a standard, provided the proportion of the nutrient in the plant derived from this standard is determined. The mathematical expression of this relationship is as follows:

$$A = \frac{B(1 - y)}{y}$$

where A = amount of nutrient available in the soil; B = amount of nutrient in the standard; y = proportion of the nutrient in the plant derived from the standard.

CRITERIA FOR THE CHARACTERIZATION OF KAOLINITE, HALLOYSITE, AND A RELATED MINERAL IN CLAYS AND SOILS

LUIS BRAMAO, J. G. CADY, S. B. HENDRICKS, AND MAX SWERDLOW

U. S. Department of Agriculture¹

Received for publication August 22, 1951

Kaolin minerals are important constituents of the clay fraction of many of the red and yellow soils. Kaolinite and halloysite are the members of the group commonly present, but the two are not differentiated in most mineral identification work on soil clays. Both minerals have the same chemical composition, approaching $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and essentially the same basic structure but differ in the size of the crystallite units developed and in the degree of randomness of stacking of the alumina-silica sheets. Halloysite probably originates through dehydration of the hydrated form $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ (endellite) (1), and this contributes to certain irregularities in its structure. It always contains a small amount of excess water above the structural formula requirement, and this increases the disorder in the stacking of the sheets (2, 4, 9). The shape of halloysite crystals as seen in the electron microscope has been variously described as laths (1) or rods and tubes (2) but is considered morphologically different from the hexagonal plates of kaolinite (7).

The common procedure for characterizing soil clays is based on a comparison of the results of physical and chemical determinations with the results of the same determinations on pure mineral specimens. In the work here described differential thermal analysis, powder x-ray diffraction analysis, and electron microscopy observations were used to obtain independent evaluations subsequently correlated. Determinations were made on the following mineralogical specimens of kaolinite: two English china clays; two Florida plastic kaolins; two from Dry Branch, Georgia; one each from Franklin, N. C., Woodleaf, N. C., Texas, and Gerez and S. Gens, Portugal. Halloysites were from Black Hills, S. D.; Eureka, Utah; Real County, Texas; Lawrence County, Ind.; Woodleaf, N. C., Nevada; and Melilla, Spanish Morocco. The samples of clay separated from red soils of Portugal and the United States of America are listed in table 2. Attention was concentrated on the kaolin mineral component of the soils. Other minerals were noted but were not considered directly except as diluents or contaminants.

¹ The senior author (L. B.) is affiliated with Estacao Agronomica Nacional, Sacavem, Portugal; two authors (J. G. C. and S. B. H.) are with the U. S. Department of Agriculture, Beltsville, Md.; the fourth author (M. S.) is with the National Bureau of Standards, Washington, D. C.

The authors are grateful to R. S. Dyal for his assistance in the differential thermal analysis work. The senior author is indebted to the Instituto Para A Alta Cultura De Portugal; The Rockefeller Foundation; R. M. Salter, F. W. Parker, and L. T. Alexander of the Bureau of Plant Industry, Soils, and Agricultural Engineering; and E. U. Condon, H. In-sley, and H. F. McMurdie of the National Bureau of Standards for support, encouragement, and hospitality in the course of this work.

DIFFERENTIAL THERMAL ANALYSIS

The considerable hydroxyl content of the kaolin minerals makes them particularly well suited for analysis by LeChatlier's differential thermal method. Since the structural layers are identical in these minerals, the amount of heat absorption and the temperatures at which water is driven off are closely similar. Several workers (8, 11) have noted, however, that the differential thermal analysis curves (referred to hereafter as D.T.A.) of halloysite are characteristically asymmetrical with a very steep slope on the recovery side of the main endothermic peak. In this study also it was found that halloysite gave, without exception, the asymmetrical type of curve later illustrated in figure 2D, E, and F.

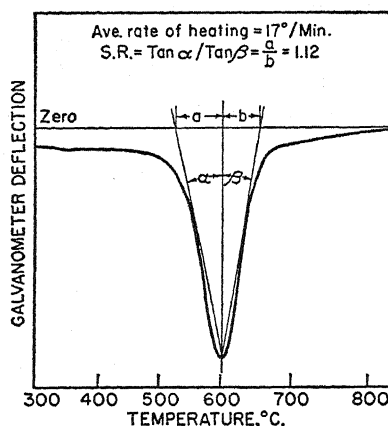


FIG. 1. CONSTRUCTION FOR DETERMINING THE SLOPE RATIO FROM THE MAIN ENDOTHERMIC PEAK, ILLUSTRATED ON THE D.T.A. CURVE OF KAOLINITE FROM DRY BRANCH, GEORGIA

An electron micrograph of this well-crystallized kaolinite is shown in figure 4B.

A number of D.T.A. curves of kaolin minerals were obtained with an apparatus previously described (10) and by the same general procedure except that the sample was tamped into the holder without being weighed. The shape of a curve was characterized by the ratio between the slopes of the tangents drawn, as shown in figure 1, to the ascending and descending parts of the curve. For this purpose the slope ratio is here defined as $\tan \alpha / \tan \beta = a/b$. This method was adopted as being more precise than determining the ratio of the slopes at the inflection points, which is perhaps of greater physical significance.

Values for the slope ratio of eleven kaolinites varied from 0.78 to 2.39 with a mean value of 1.55 and an average deviation from the mean of 0.31. Seven samples of halloysites gave values between 2.50 and 3.80 with a mean value of 3.11 and an average deviation from the mean of 0.40. The minimum slope ratio for kaolinite was given by an English china clay, pharmaceutical grade, which the electron micrographs showed to be very coarsely crystalline (fig. 4A), whereas very finely divided kaolinite from Hawthorne, Florida (fig. 4C) gave a slope ratio of 2.00. This latter sample, as well as several other kaolinites, contained a

minor amount of halloysite, but presumably this did not modify the shape of the D.T.A. curve.

Values for the slope ratios taken from 24 published D.T.A. curves for kaolinite (11) varied from 1.00 to 1.75 with a mean value of 1.43 and an average deviation from the mean of 0.18. Seven samples of halloysite varied from 2.60 to 4.00 with

TABLE 1
Differential thermal analysis, slope angles, slope ratios, and particle sizes for some clay fractions

CLAY MINERAL	COARSE			MEDIUM			FINE ($<0.2 \mu$)		
	α	β	S.R.*	α	β	S.R.	α	β	S.R.
	degrees	degrees		degrees	degrees		degrees	degrees	
Kaolinite (Hawthorne).....	12.3	9.7	1.34	10.9	5.9	1.90	9.3	4.2	2.36
Kaolinite (English china)...	13.0	11.2	1.07	9.2	6.5	1.44	9.3	5.0	1.87
Halloysite (indianaite).....	14.8	5.3	2.81	13.5	4.8	2.85	11.3	3.7	3.00

* S.R. = Slope ratio.

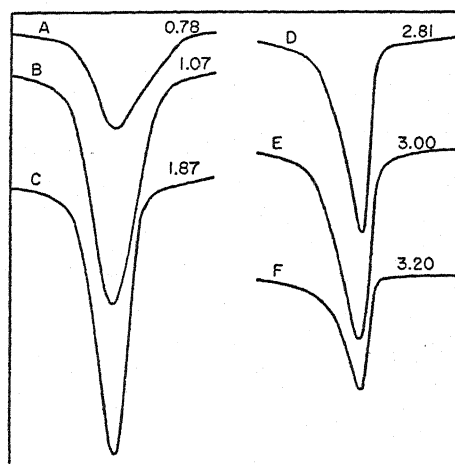


FIG. 2. SAMPLE D.T.A. CURVES SHOWING SLOPE RATIOS FOR KAOLINITE, HALLOYSITE, AND A SOIL KAOLIN

A. Very coarsely crystalline English china clay; B. Another English china clay, coarse fraction (table 1); C. Fine fraction; D. Halloysite (indianaite), coarse fraction (table 1); E. Fine fraction; F. Clay from Beja soil.

a mean value of 3.25 and an average deviation from the mean of 0.39. Despite inherent differences among the several D.T.A. apparatus and the differences in the heating rates used, the slope ratios of kaolinite and halloysite fell into two distinct groups.

The suggested dependence of the slope ratio upon particle size was tested for English china clay, Hawthorne kaolin, and halloysite (indianaite, fig. 4F).

These were fractionated by sedimentation into coarse, medium, and fine fractions, the last being less than 0.2μ in size. Results obtained from D.T.A. of these fractions are shown in table 1. Some of the D.T.A. curves from which these results were obtained are reproduced in figure 2 to illustrate the variation in shape, that is, the inverse variation of slope ratio with particle size. In kaolinites the fractionation led to separation of individual particles, whereas in indianaites the coarser material was comprised of aggregates of fine particles. A halloysite from Real County, Texas (fig. 4E) that contained much larger individual particles than did the Hawthorne kaolinite gave a slope ratio of 2.66 as compared with 2.36 for the fine fraction of the Hawthorne clay mineral. The conclusion is drawn that halloysites have inherently a higher value of the slope ratio than do kaolinites of equivalent particle size. This might be expected from imperfectness of halloysite crystals, leading to greater nucleation upon decomposition. In both cases, however, there is an effect of particle size. Thus the possibility exists of a very finely divided kaolinite having a slope ratio in the range of halloysites, but the inverse possibility of a halloysite having a slope ratio below 2.50, in the kaolinite range, would appear to be unlikely.

The dehydration reaction involved in D.T.A. has been discussed (13). In its initial stages it is a first order reaction, the rate of which is determined by the rate of formation of reaction centers, that is, the rate of nucleation. From these centers, the dehydration reaction spreads at the interfaces between the starting material and its decomposition product until an entire crystal is altered. The smaller the crystal size for a particular material, the greater will be the number of nuclei required for decomposition of a given weight of material, or correspondingly the greater the time over which nucleation controls the rate of the reaction. Equivalently, the larger the particle size, the greater the amount of material decomposed per nucleus. Apparently for this reason the amount of the material decomposed by the time the maximum lag in temperature is reached varies inversely with crystal size.

The return to zero deflection is determined by exhaustion of material, and this accordingly is more rapid for small particles than for large particles. The result is that smaller values of β are given by the smaller crystals. Thus a small value of β may indicate either a kaolinite of small particle size or a halloysite. Though β may appear to be an important determinant, it cannot be used alone as a criterion in distinguishing kaolinite from halloysite. The slope ratio, however, becomes the more decisive indicator since it is generally greater for halloysite than for kaolinite, as shown in table 1.

X-RAY DIFFRACTION ANALYSIS

The characteristics of the x-ray powder patterns of kaolinite and halloysite and structural reasons for the differences in the patterns have been discussed (3, 5). Kaolinite has a (001) spacing with $d = 7.15\text{\AA}$, and in all the mineralogical specimens examined both the (001) and (002) reflections were sharp and intense. Kaolinites also show reflections of (hkl) planes in which $h + k$ is an even number, though some of these reflections may be weakened by preferred orientation of the basal plane or irregularities in the crystal structure. The presence and rela-

tive strength of these (hkl) reflections are as informative about the identity and structural perfection of the minerals as are the spacings, shapes, and intensities of the ($00l$) reflections. The (001) spacing of halloysite may range from 7.25Å. to 7.5Å., and the interference maximum is rather broad and weak. The second order reflection, (002), is usually less intense than the (020) reflection, and reflections attributed to (hkl) planes are lacking. The diffraction pattern is that of a random superposition of two-dimensional gratings. Between completely ran-

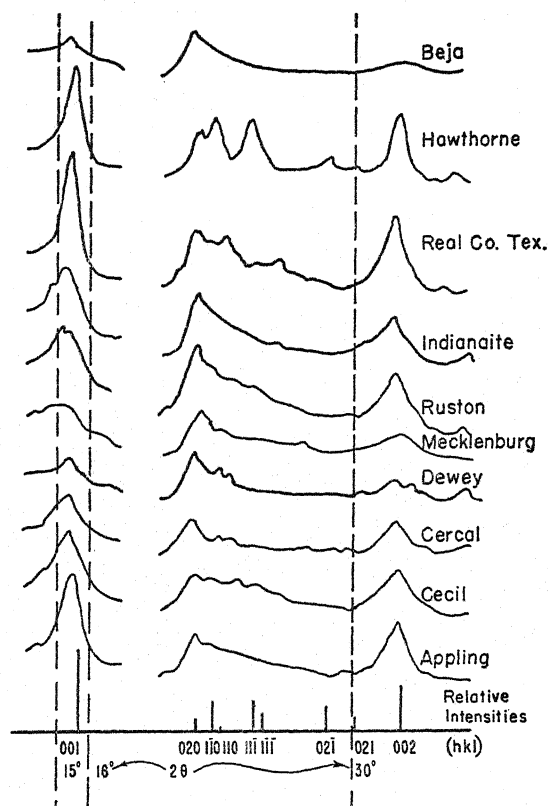


FIG. 3. TRACINGS OF PARTS OF THE X-RAY DIFFRACTION PATTERNS OF KAOLINITE, HALLOYSITE, AND SOIL CLAYS

dom halloysite and well-organized kaolinite are apparently minerals of various degrees of randomness (5).

The x-ray powder diffraction patterns of the clays and soils were obtained with the North American Philips Geiger-counter spectrometer, type 12021. The ground, dry samples were packed in an aluminum holder according to a procedure which provides a specimen surface comparatively free from preferred orientation (12). Tracings of parts of x-ray diffraction patterns of a kaolinite and two halloysites are illustrated in figure 3.

The kaolinites included showed variations in their x-ray powder patterns which

could be related to differences shown by the other methods used in this study. The English pharmaceutical grade kaolinite, which had uniform, large crystals, always showed greatly enhanced basal plane reflections in spite of all efforts to produce random orientation. Interference maxima arising from other planes in the crystals were correspondingly weak. The observed relative intensity of the basal plane (00 l) reflections was increased severalfold over the calculated theoretical intensity in most of the kaolinites studied. The degree of enhancement was directly related to particle size. The specimens that had the small slope ratios (larger particle size) had the stronger, sharper (00 l) reflections. The Hawthorne kaolinite gave an x-ray powder pattern with relative intensities very close to the calculated theoretical intensities (3). Smoothing the surface of the specimen or other treatments that produced strong orientation in other kaolinite specimens did not produce enhanced basal plane reflections.

The indianaites and most of the other halloysites, even when smoothed, showed no evidence of preferred orientation. Intensities and spacings of basal plane reflections varied somewhat, probably because of water between the structural layers, for the interference maxima could usually be sharpened and the spacing brought down to 7.25Å. by heating specimens at 200°C. for a few hours.

The halloysite from Real County, Texas, which the electron microscope showed to be composed of unusually large, well-formed crystals, gave sharp (001) and (002) reflections with intensities indicating some preferred orientation. This material had a smaller (001) spacing than other halloysites ($d = 7.20\text{Å.}$) and showed reflections corresponding to spacings $d = 4.28\text{Å.}$ and 4.05Å. , which were not present in other halloysite or kaolinite patterns. No impurities were noted by electron microscopy.

These variations in the intensities of (00 l) reflections serve as a warning against too free use of this intensity as a quantitative measure of the kaolinite percentage in mixtures. Mixtures were made of the china clay and halloysite in several proportions. The halloysite could not be identified in the mixtures except when the proportion was as high as 4:1, and then its presence was only suggested by a change of the (001) reflection to an average spacing of 7.4Å. The intensity of this reflection was decreased with each increment of halloysite, but when dealing with unknowns, one would not know whether the intensity was due to an admixture or to the crystal size and randomness of the kaolinite itself.

ELECTRON MICROSCOPY

The electron microscope, like the conventional light microscope, is primarily designed to furnish enlarged images of minute objects or specimens interposed in the path of the radiant energy. Variations of the electron scattering power in different parts of the specimen give rise to variations of intensity in the corresponding parts of the image. These electron optical images provide exact information about the shape and size of finely divided matter and a limited amount of other information about the physical and chemical structure of the object. The practical resolving power (better than 100Å.) of the R.C.A. Type EMU 50KV instrument used in this study offers an accurate visual method for delineating

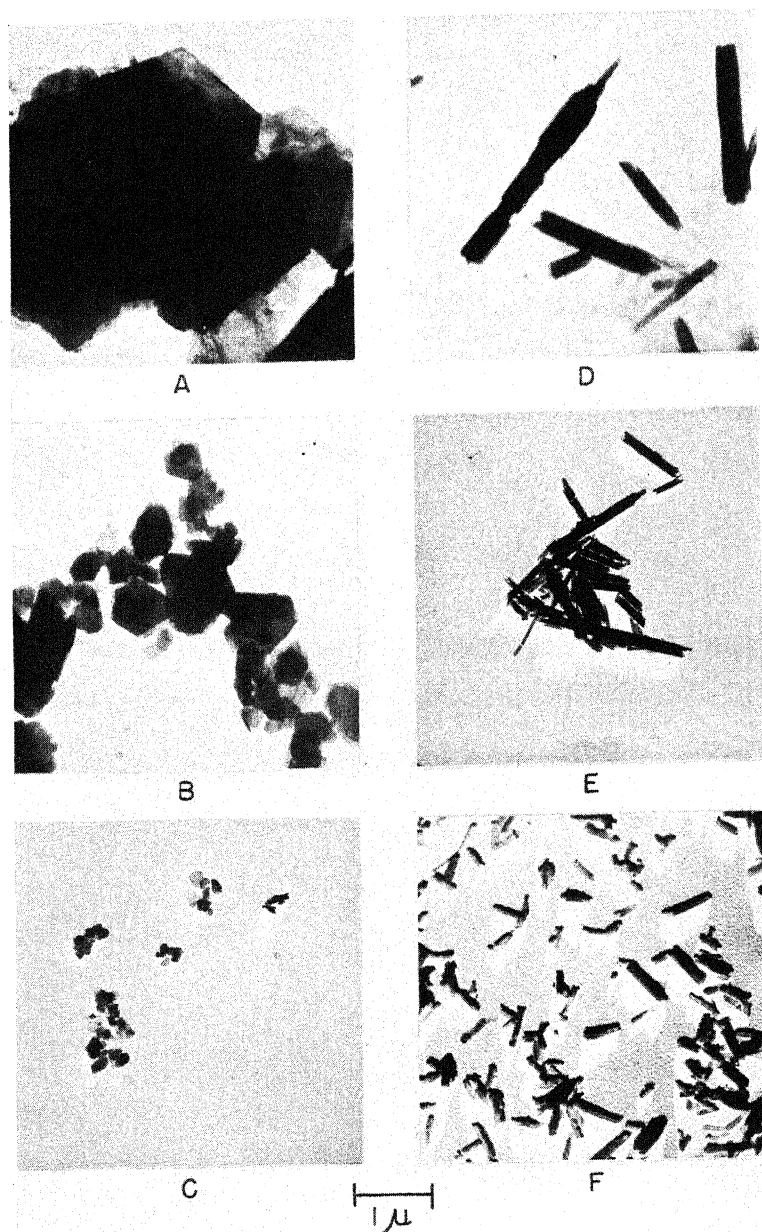


FIG. 4. ELECTRON MICROGRAPHS OF KAOLINITE AND HALLOYSITE, ILLUSTRATING VARIATION IN SIZE AND SHAPE

A. Kaolinite, English china clay; B. Kaolinite, Dry Branch, Georgia; C. Kaolinite, Hawthorne, Florida; D. Halloysite, Black Hills, South Dakota; E. Halloysite, Real Co., Texas; F. Halloysite, Lawrence Co., Indiana (indianaite).

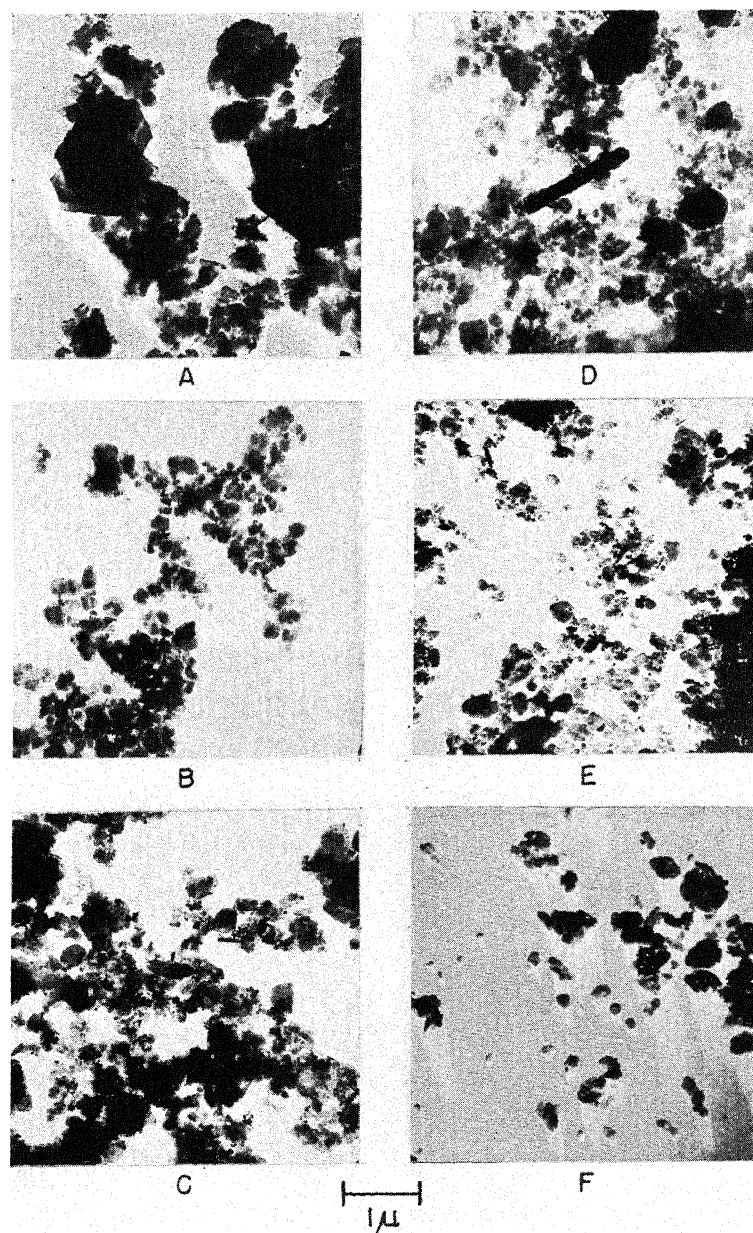


FIG. 5. ELECTRON MICROGRAPHS OF SOIL CLAYS

A. Cercal (Portugal); B. Greenville (U. S. A.); C. Cecil (U. S. A.); D. Decatur (U. S. A.); E. Ruston (U. S. A.); F. Beja (Portugal).

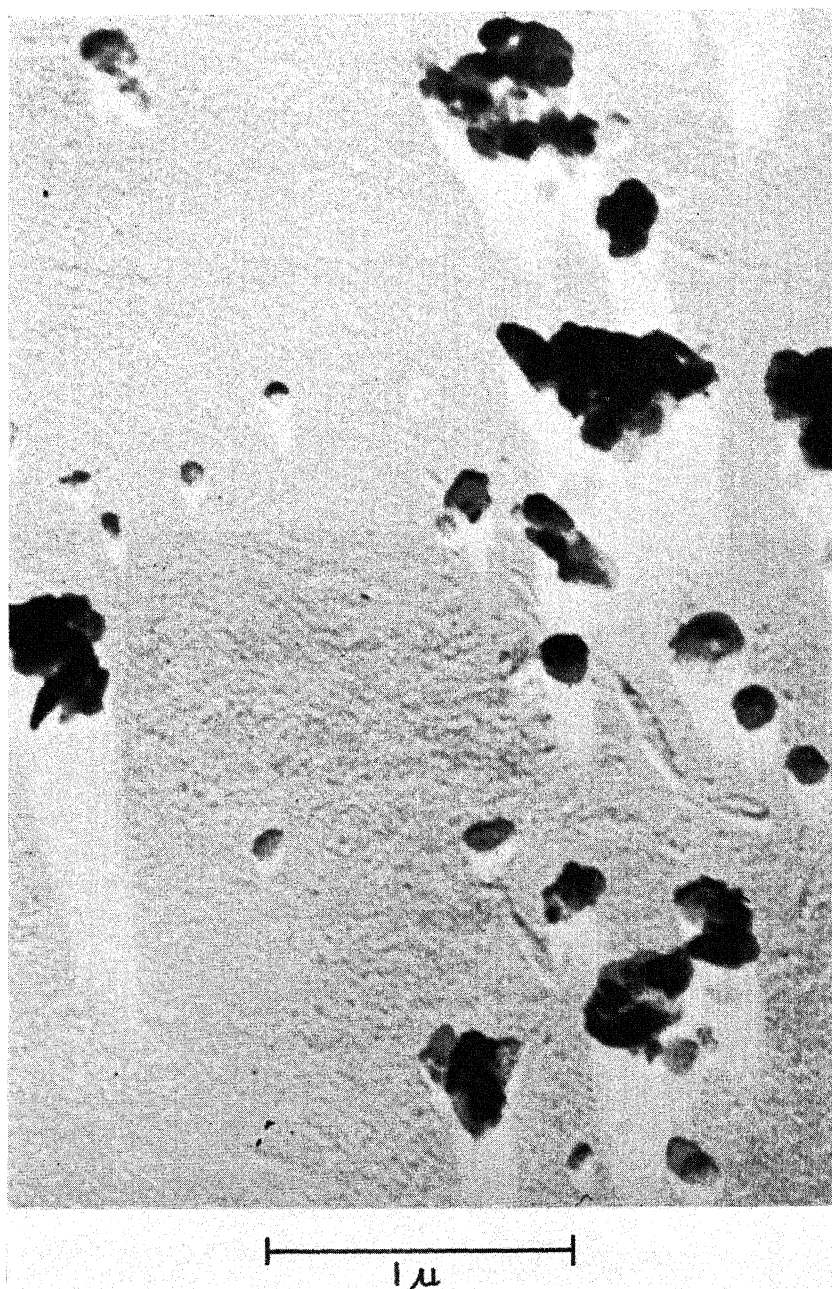


FIG. 6. ENLARGEMENT OF PART OF THE ELECTRON MICROGRAPH IN FIGURE 5F, BEJA SOIL CLAY, ILLUSTRATING MORPHOLOGICAL DETAIL OF THE CLASS 3 KAOLIN MINERAL

and comparing the morphologies of the particles found in clays and soils. The main limitations lie in the interpretations of the observations and in the difficulties of specimen preparation. When electron microscopical examinations are made in light of information gained from other studies, such as x-ray diffraction and differential thermal analyses, identification of the kaolin constituents in clays and soils is more certain.

Careful controls and the use of at least eight separate specimens from each sample overcome most of the limitations imposed by the difficulties of attaining perfect dispersions of truly representative samples of each of the soils and clay minerals. The specimens were prepared by dispersing a suitable amount of the material in clean water and allowing drops of the suspended particles to dry on a collodion or Formvar (polyvinyl formal) film supported by a $\frac{1}{8}$ -inch 200-mesh screen. The specimens were scanned and electron micrographs of characteristic fields were obtained directly at a magnification of 10,000 diameters (figs. 4 and 5). Figure 6 is a four-fold enlargement of part of figure 5F. Metallic shadow casting (15) was used to provide additional contrast and a three-dimensional aspect to the surfaces and particles observed. This was done by slowly evaporating about 75 mgm. of pure electrolytic chromium metal pieces from a conical tungsten-wire basket at a pressure of less than 10^{-5} mm. of Hg.

As the atoms of chromium condense, elevations and depressions on the surface of the specimen cast shadows characteristic of its contours. Where no metal is deposited, transmission of the incident beam of electrons in the microscope is maximum, and where thick elevations occur, electron scattering is maximum and little or no electrons are transmitted by the specimen. The shadows cast are approximately four times the height of the particles causing them. Positive prints are shown in figures 4, 5, and 6. They represent the images as seen in the microscope; black indicates electron optically opaque material, and white represents the transparent parts of the specimen. Both the shadowed and unshadowed micrographs may be interpreted on this basis. In electron microscopy, the distinctive crystal morphology—the hexagonal plates of kaolinite and the rodlike particles of halloysite—is the recognized criterion for their differentiation.

Hydrated halloysite and halloysite appear to have the same cylindrical morphology, though considerable difference is registered in the x-ray diffraction pattern of these two minerals (6). The hydrated halloysite from Eureka, Utah, was observed in the electron microscope before and after the transition to halloysite produced by heating at 350°C. for 2 hours, and the crystals were found to be morphologically similar. Possibly, a fully hydrated halloysite has never been observed in the electron microscope because of the vacuum required in the specimen chamber and the heat produced by electron beam bombardment (1, 2).

APPLICATION OF THE CRITERIA TO SOIL CLAYS

Clays separated from sixteen soils, classified chiefly as red and yellow podzolic, reddish brown lateritic, and red Mediterranean, from Portugal and the eastern United States of America were studied by the three methods to test the criteria.

Many of the samples were examined both before and after removal of the free iron oxides by a modification of the photochemical oxalate reduction procedure (14). The D.T.A. curves showed that all the clays contained between 30 and 65 per cent of a kaolin mineral. Illite, montmorillonite, gibbsite, quartz, and limonitic minerals were present in various samples and accounted for the remainder of the composition.

The slope ratios obtained from the D.T.A. curves of the soil clays are shown in table 2, and an example of such a curve is figure 2F. A kaolin endothermic peak with a relatively high value of the slope ratio is a characteristic feature of many clays from soils. Positive identification of kaolinite can be made in those samples having a slope ratio less than 2.50, provided kaolin is a predominant mineral present. Kaolin clays having slope ratios higher than 2.50 are not necessarily halloysites. For example, Greenville with a slope ratio of 3.00 is chiefly kaolinite by the criteria of x-ray diffraction and electron microscopy (fig. 5B). The explanation may lie in the combined effects of small particles and poorly organized crystals. The majority of the soil clays having slope ratios higher than 2.50 contain either mixtures of typical halloysite and kaolinite, such as Cecil (fig. 5C), or very fine grained, poorly organized kaolin, such as Beja (figs. 5F and 6).

Soil clays, such as, Albergaria, Sagres, and Decatur (fig. 5D) with slope ratios slightly below 2.50 are diluted and contaminated by the presence of large proportions of other minerals such as illite. In such instances, identification is uncertain. Thus the slope ratios obtained from the main endothermic peak in the D.T.A. curves applied to the characterization of the kaolin-containing soils provide information which, for the present, cannot always be completely evaluated.

Tracings of parts of some x-ray diffraction patterns are illustrated in figure 3. The patterns were studied and classified according to: 1. Spacing, shape and intensity of the (00 l) interference maxima. 2. Relative intensity of the (020) reflection and (00 l) reflections; since other platy clay minerals contribute to scattering in the region of (020) at 4.47Å., their presence must be considered. 3. Presence and intensity of ($hk0$) and (hkl). None of the soil clays had basal plane spacings as small as those of pure kaolinite and none had well-developed (hkl) interference maxima. When these criteria were applied to the x-ray diffraction patterns of the soil clays, the following types were apparent:

I. *Kaolinite predominant.* The basal plane reflections are strong, rather sharp with a spacing about 7.25Å. The intensity of (002) is greater than that of (020), and there is at least some suggestion of (hkl) reflections. Some examples are Appling, Cecil, Cercal, and Greenville.

II. *Halloysite predominant.* The basal plane reflections are broad, with rather low intensities and the spacing is 7.3Å. to 7.45Å. The intensity of (020) is stronger than that of (002), and (hkl) reflections are essentially absent. Illite and montmorillonite are not evident. Some examples are Mecklenburg, Orangeburg, and Ruston.

III. *Indefinite.* Most soil clays of this type contain appreciable amounts of other clay minerals. The basal plane reflections are broad, relatively weak, rang-

ing from spacings 7.25Å. to 7.45Å. The kaolin (hkl) reflections are weak or absent. Presence of illite and sometimes montmorillonite makes interpretation of intensities of (020) difficult. This mixture may include randomly organized kaolin or mixtures of kaolinite and halloysite. Some examples are Albergaria, Dewey, and Sagres.

In table 2 the soils are classified according to these three types of x-ray powder patterns. Results of electron microscopical observations are shown in the last column. These are conclusive when definite kaolinite hexagons or halloysite cylinders are observed—class 1 and 2, respectively.

Electron microscopical observations showed that the crystal size of kaolin minerals in soil clays is usually much smaller than that of the kaolin minerals from commercial deposits and mineralogical specimens (compare figures 4 and 5). The soil clays seldom attain the same degree of perfection of crystal form as do those from natural clay deposits. In some soils, such as Cercal (fig. 5A) and Cecil, the minerals have been inherited from parent materials that contained well-crystallized kaolinite, and these soils retain the mineral in a fairly well preserved condition. The kaolin mineral present in soil clays is commonly associated with other minerals.

The soil clays containing a predominant proportion of kaolin mineral gave evidence of particles of three morphological classes. These are: 1. hexagonal plates; 2. cylindrical or rodlike particles; 3. irregular layered particles having curved surfaces.

The first of these is recognized as kaolinite and the second as halloysite, both similar in morphology to the mineralogical specimens. The third class (fig. 6) as shown by electron microscopy (figs. 5E, 5F, and 6) exhibits some features of both halloysite and kaolinite of mineralogical specimens but is sufficiently distinct to be recognized and is not necessarily a transitional form. This class has more poorly formed particles. In general, they appear "puffier" and thicker, as shown by shadow-casting, than do flat kaolinite plates equivalent in area but not so thick as would be required if they were segments of a rod. The surfaces are not so smooth as those of kaolinite and halloysite when seen in shadow-cast material. They might be described as slightly porous and roughened in texture. The particle outline often tends toward a hexagonal shape but with rounding of the faces. The particles show a marked tendency to agglomerate. In this, there is some similarity to the flocculation characteristics of illite, but in many of the soil samples no illite is indicated by x-ray diffraction.

Definite identification of kaolinite in soil clays can be made by the D.T.A. and x-ray criteria subject to the limitations described. Neither method, however, is completely satisfactory for distinguishing halloysite in soil clays, since some finely divided kaolin material might have a slope ratio greater than 2.50, a somewhat enhanced value of (001) spacing, and give no (hkl) reflections and still not have the rod and tubelike particles of halloysite. Such material appears in Ruston, Mecklenburg, and Orangeburg soils. Soil clays showing a high slope ratio and a halloysitic x-ray diffraction pattern might contain cylindrical halloysite alone, a mixture of hexagonal kaolinite and cylindrical halloysite, or the

fine-grained, poorly organized mineral which was called class 3 and which may be the kaolin mineral of fireclay (5).

The enhancement of the (001) spacing observed in many of the soil clays which contain platy hexagonal particles strongly suggests that soil kaolinites can have interplanar spacings of (001) greater than 7.25Å., indicative of material interleaved between the structural sheets.

TABLE 2
Summary of observations on some soil clays

SOIL GROUP	SOIL SERIES	LAB. NO.	PARENT MATERIAL	D.T.A. SLOPE RATIO	X-RAY DIFFRACTION PATTERN TYPE	ELECTRON MICROSCOPICAL MORPHOLOGICAL CLASS*
Red Mediterranean soils, Portugal	Albergaria	298	Soft limestone	2.33	III	3
	Beja	410	Shale	3.20	II	3, 2
	Cercal	777	Sandstone	1.83	I	1, 2
	Marinha	401	Hard limestone	2.37	III	?
	Sagres	29	Hard limestone	2.26	III	3
Red-yellow podzolic soils, U.S.A.	Appling	C-836	Granite	1.83	I	1, 2
	Cecil	C-5065	Gneiss and granite	3.11	I	1, 2
	Dewey	C-120	Hard limestone	2.16	III	3, 1
	Fullerton	C-109	Cherty limestone	2.00	III	1, 3
	Norfolk	—	Coastal Plain sediments	2.35	I	3, 1
	Orangeburg	C-289	Sands and	2.90	II	3
	Ruston	—	Sandy clays	3.18	II	3
	Decatur	C-7180	Hard limestone	2.21	III	1, 3, 2
Reddish brown latosols, U.S.A.	Greenville	C-1067	Coastal Plain sediments	3.00	I	1, 2
	Mecklenburg	—	Diorite, gabbro	2.75	II	3, 2
	Red Bay	—	Coastal Plain	2.81	I	3, 1
		—	sediments			

* The symbols I, II, III refer to the three types of x-ray diffraction powder patterns described in the text. The symbols 1, 2, 3 refer to the three electron microscopical morphological classes described in the text. The symbol ? indicates material not identifiable by these criteria. The kaolin minerals in this column are listed in order of their relative abundance.

The small particle size and evident poor crystallinity of much of the soil kaolin are results of the weathering conditions in soils. Soils are subject to wetting and drying cycles; a kaolinite crystal may begin to synthesize in one part of the cycle, and its growth may be interrupted or retarded during another part. The next increment of crystal growth might be more hydrous, or have a slightly different chemical composition and physical structure. Soil formation is characterized by the simultaneous presence of a large number of free ions and colloidal systems; the latter, particularly the hydrous oxides of aluminum and iron, may well affect the development of clay mineral crystals. Where halloysite and kaolin-

ite can grow undisturbed in an ideal environment, they can attain their characteristic euhedral forms. Where weathering conditions are dynamic and reflect the interplay of a host of variables, as in soils, perfect crystal formation would be only fortuitous. From one point of view, halloysite may be considered a special form of kaolinite; one that has been warped and strained by the presence of excess water molecules. The possibility of a clay mineral genesis sequence from hydrated halloysite to halloysite to fine, random kaolinite should not be overlooked. The common occurrence of the material described as morphological class 3 indicates that it may be an equilibrium form peculiarly developed in a soil environment.

CONCLUSIONS

The shape of the main endothermic peak on the D.T.A. curve of kaolin minerals is related to particle size and degree of crystalline perfection. When shape is expressed as the ratio of the tangents of the angles of slope of the two sides of the peak (fig. 1), the slope ratios of mineralogical specimens fall into two groups. Halloysites have slope ratios greater than 2.5, whereas kaolinites give values generally between 1.2 and 1.8. Slope ratio can be used as a positive criterion to identify kaolinite.

Presence of (*hkl*) x-ray reflections with *h*, *k*, or *l* not equal to zero and of (001) reflections from interplanar spacings from 7.15 to 7.20Å. is also a definite kaolinite criterion, particularly when the crystals can be oriented by smoothing the surface of the specimen. The tendency of crystals to orient in mounting prohibits use of x-ray diffraction for quantitative estimates of kaolinite.

Electron microscopical observation of hexagonal plates of kaolinite and the cylindrical forms of halloysite are further definite criteria. For mineral specimens, the three methods used were entirely consistent.

Hexagonal-shaped kaolinite was observed in many soils. Cylindrical-shaped halloysite was observed in some soils as a minor constituent. The kaolin mineral in many soils is in the form of small particles and is poorly crystallized, with random stacking of structural layers, having some interleaving of water or the interlayer spacing disturbed in other ways. The latter kind of soil kaolin has certain structural properties of halloysite according to D.T.A. and x-ray diffraction; it exhibits features between that of halloysite and kaolinite according to electron microscopy. It is, however, sufficiently different to represent a separate third morphological class of kaolin mineral and possibly represents an end form rather than a transitional one. The kaolin mineral present in some soil clays is commonly associated with other minerals that act as diluents or contaminants. In such cases the criteria established by the three methods can provide clues but not complete identification.

REFERENCES

- (1) ALEXANDER, L. T., ET AL. 1943 Relationship of the clay minerals halloysite and endellite. *Amer. Mineral.* 28: 1-18.
- (2) BATES, T. F., HILDEBRAND, F. A., AND SWINEFORD, A. 1950 Morphology and structure of endellite and halloysite. *Amer. Mineral.* 35: 483-484.

- (3) BRINDLEY, G. W., AND ROBINSON, K. 1946 The structure of kaolinite. *Mineral Mag.* 27: 242-253.
- (4) BRINDLEY, G. W., AND ROBINSON, K. 1946 Randomness in the structure of kaolinitic clay minerals. *Trans. Faraday Soc.* 42B: 198-205.
- (5) BRINDLEY, G. W., AND ROBINSON, K. 1947 An X-ray study of some kaolinitic fire-clays. *Trans. Brit. Ceram. Soc.* 46: 49-59.
- (6) BRINDLEY, G. W., AND GOODYEAR, J. 1948 X-ray studies of halloysite and metahalloysite: II. *Mineral Mag.* 28: 393-428.
- (7) DAVIS, D. W., ET AL. 1950 Electron micrographs of reference clay minerals. Amer. Petroleum Inst. Proj. 49, *Prelim. Rpt. 6* (Columbia Univ., New York).
- (8) DEAN, L. A. 1947 Differential thermal analysis of Hawaiian soils. *Soil Sci.* 63: 95-105.
- (9) HENDRICKS, S. B. 1938 On the crystal structure of the clay minerals: dickite, halloysite, and hydrated halloysite. *Amer. Mineral.* 23: 295-301.
- (10) HENDRICKS, S. B., AND ALEXANDER, L. T. 1939 Minerals present in soil colloids: I. *Soil Sci.* 48: 257-271.
- (11) KERR, P. F., KULP, J. L., AND HAMILTON, P. K. 1949 Differential thermal analyses of reference clay mineral specimens. Amer. Petroleum Inst. Proj. 49, *Prelim. Rpt. 3* (Columbia Univ., New York).
- (12) MCCERRY, G. L. 1949 Improved mount for powdered specimens used on the Geiger-counter X-ray spectrometer. *Jour. Amer. Ceram. Soc.* 32: 141-146.
- (13) MURRAY, P., AND WHITE, J. 1949 Kinetics of the thermal dehydration of clays. *Trans. Brit. Ceram. Soc.* 48: 187-206.
- (14) SCHOFIELD, R. K. 1949 Effect of pH on electric charges carried by clay particles. *Jour. Soil Sci.* 1: 1-8.
- (15) WILLIAMS, R. C., AND WYCKOFF, R. W. G. 1944 The thickness of electron microscope objects. *Jour. Appl. Phys.* 15: 712-715.

USE OF CA45 LABELED CALCIUM CARBONATE IN DETERMINING PROPORTIONS OF NATIVE AND ADDITIVE CALCIUM IN LYSIMETER LEACHINGS AND IN PLANT UPTAKE

HENRY C. HARRIS, W. H. MACINTIRE, C. L. COMAR, W. M. SHAW,
S. H. WINTERBERG, AND S. L. HOOD

University of Tennessee and U. S. Atomic Energy Commission¹

Received for publication March 1, 1951

In conducting conventional lysimeter studies (5, 6, 10) on soil liming before the advent of labeled calcium, it was customary to assume that enhancements in calcium outgo came from the additive materials, although it was thought possible that a fraction of the increase might come from the calcium supply native to the soil. Moreover, there could be no distinction as to the relative amounts of the calcium that plants derived from the additive and natural supplies in a limed soil. Now, through the use of radio-calcium, it is possible to determine the proportions of the native calcium to the added calcium in the leachings from a limed soil and in the crops grown on the soil.

This paper presents comparative findings from simultaneously conducted lysimeter and greenhouse experiments in which Ca45 was included in the incorporations of precipitated calcium carbonate.

MATERIALS AND METHODS

The properties of Hartsells fine sandy loam and of Claiborne silt loam used are listed in table 1. Facilities for determining the type of clay minerals in these soils were not available, but Pearson and Ensminger (9) have given the mineralogical composition of the clay separates from the Hartsells and Decatur series, the latter being related to the Claiborne. The clay minerals of both soils were kaolinitic.

About 1,300 gm. of precipitated CaCO_3 was prepared for the experiments to contain approximately $5.4 \mu\text{c}$ of Ca45 per gram. It was prepared by adding Ca45Cl_2 to a water solution of c.p. CaCl_2 , precipitating the calcium as carbonate through injection of gaseous ammonia, and then bubbling CO_2 into the solution, under $1\frac{1}{2}$ atmosphere, until precipitation was virtually complete. The precipitate was water-washed, dried, pulverized to pass a 100-mesh screen, and its radioactivity determined. Thus prepared, the Ca45CO_3 was mixed in the soils at rates of 0, 1, 2, 3, 4, and 5 thousand pounds per acre for several lysimeter and greenhouse experiments that were conducted simultaneously on both soils, as in previous studies (7, 10).

A single uncropped lysimeter of 1/20,000 acre (100 pounds of soil per tank)

¹ Cooperative study of University of Tennessee—Atomic Energy Commission Agricultural Research Program, Oak Ridge, and chemistry department, Tennessee Agricultural Experiment Station, Knoxville. The Ca 45 was obtained from the Oak Ridge National Laboratory through allocation by the U. S. Atomic Energy Commission. H. C. Harris was a research fellow of the Oak Ridge Institute of Nuclear Studies.

was used for each of the liming rates on both soils. The soil was compacted in a layer in the lysimeter tank approximately 10 inches deep on a base of ground quartz. The carbonate incorporations were made November 11, 1949, and the drainage waters were collected and analyzed nine times during the ensuing year.

Aliquots of the leachings were evaporated, and the resultant residues were taken up with dilute HCl. Total calcium was determined in aliquots of the HCl solutions through precipitation as the oxalate and permanganate titration. Radioactivity measurements by means of a thin-window Geiger counter were made on aliquots of the acid solutions which were evaporated to dryness in 50 mm. petri dish bottoms (2, 4). The usual corrections for self-absorption and decay were made. After one year, the soil of each lysimeter was analyzed for residual carbonates, and the pH values of the soil in water suspension were determined by means of the glass electrode.

TABLE 1
Properties of Hartsells and Claiborne soils

DETERMINATIONS*	HARTSELLS FINE SANDY LOAM	CLAIBORNE SILT LOAM
Exchange capacity at pH 7.....me.	12.2	11.4
Exchangeable Ca.....me.	1.2	4.5
Exchangeable Mg.....me.	0.3	1.1
Exchangeable H.....me.	10.7	5.8
Base saturation.....per cent	12.3	49.1
pH values in H ₂ O.....	4.5	5.7
Organic matter.....per cent	4.7	2.8

* Exchangeable Ca and Mg were determined by means of ammonium acetate extraction and leaching of 10 gm. soil with 250 ml.; exchangeable H was determined by replacement with 250 ml. 0.5 M neutral Ca-acetate and titration of the engendered acidity with 0.1 N Ba(OH)₂ to pH 8.8; exchange capacity was through summation of the Ca, Mg, and H; and organic matter by the Walkley method (11).

A laboratory supplement to the lysimeter experiment was conducted on Hartsells soil. Unlabeled precipitated CaCO₃ was mixed at the rate of 4,000 pounds per acre into one air-dried portion of soil. The soil then was wetted with distilled water, air-dried, remixed, and the wetting and drying process was repeated. This took about 5 days, and it was known that considerable decomposition of CaCO₃ would ensue. Precipitated CaCO₃ was not incorporated into the other portion of soil. Duplicate 240-gm. portions of the carbonate-treated air-dried soil and the untreated soil were put in large beakers, and additions of the labeled CaCO₃ were made at the rates of 0 to 5,000 pounds per 2,000,000 pounds of soil. To each charge was added 350 ml. of distilled water, and the suspension was stirred intermittently for an hour. Then CO₂ was bubbled through the soil-water suspensions for 1½ hours, and the suspensions were allowed to stand overnight. The next morning the CO₂ treatment was repeated with occasional stirring for another 1½ hours. The suspension then was filtered by means of a Büchner funnel under suction. The filtrates were analyzed for calcium, total and radioactive, as described previously for the lysimeter leachates.

In the greenhouse experiment 17.6 pounds of air-dried soil was put in every glazed crock. The labeled CaCO_3 treatments of the greenhouse experiment were in triplicate, and the experiment was conducted concurrently with the lysimeter study. Whenever nonlegumes were grown, NH_4NO_3 was applied, 100 pounds per acre. Phosphorus was applied as KH_2PO_4 to all crops at the rate of 160 pounds of P_2O_5 per acre and sufficient K_2SO_4 was added to bring the K_2O up to 100 pounds per acre. These supplements were applied to all cultures at constant rate. A crop of red clover and one of rye grass were grown in parallel on each soil. These crops were sampled at intervals and harvested February 25, 1950, at approximately the maximal vegetative stage before flowering. After these two crops had been grown, the roots and stubbles were incorporated in the surface soil to a depth of about 3 inches in preparation for another seeding. Oats were then seeded to follow red clover, and rye grass was followed by crimson clover. The crops of this set were handled as were those of the first set, and the final harvests of the oats and clover were May 12 and June 1, 1950.

Samples of the plant material were ashed at 550°C . The ash was taken up in dilute HCl , and total calcium and radioactivity measurements were made on aliquots of the HCl solution in the manner described for analyses of the soil leachings.

RESULTS OF THE LYSIMETER EXPERIMENT

The analytical values for the nine different periodic samplings of the drainage waters are so similar that only the totals for the year are recorded in table 2. To illustrate how similar were the results for the different samplings, the percentages of calcium from the native soil calcium for the first set of samples from the Hartsells soil were 100, 59, 24, 12, 8, and 0, whereas the corresponding ones from the Claiborne soil were 100, 85, 77, 57, 49, and 40. The same values for the ninth sampling for the Hartsells soil were 100, 58, 31, 20, 6, and 3, and those for the Claiborne soil were 100, 80, 63, 49, 32, and 40. The only difference noted in values for the samples at different periods was that there seemed to be more calcium in the earlier leachings, the first sampling having several times as much calcium as the last sampling.

Every input of CaCO_3 resulted in an enhancement of the outgo of total calcium (table 2, column 3), and increases in input were reflected by progressive increases in outgo. Although the particular values are not listed, increases in the input of calcium caused progressive increases in the amount of additive calcium in the drainage. The percentage recovery of added calcium through drainage (table 2, column 4) was relatively constant for the Hartsells soil, but increased progressively for the Claiborne soil. The percentage of calcium in the drainage that was derived from the supplies native to the soil (table 2, column 6) decreased with increases in the incorporation of CaCO_3 . The soils functioned differently, however, as to the percentage of native calcium in the drainage. The highest rate of calcium input on the Hartsells soil decreased that percentage to virtually nil, whereas that input of CaCO_3 on the Claiborne soil decreased the value to approximately 40 per cent.

The *quantity* of native calcium in the drainage from the Hartsells soil (table 2,

column 5) decreased progressively with increases in additive calcium. On the contrary, the quantity of native calcium in the drainage of the Claiborne soil increased through the 4,000-pound incorporation. In other words, applying CaCO_3 decreased the loss of native calcium from one soil, but increased the loss from the other soil.

TABLE 2
Effect of incorporations of labeled calcium carbonate on lysimeter leachings of native and incorporated calcium from uncropped soils

LABELED CaCO_3 INCORPORATIONS PER ACRE*	FINDINGS FROM LYSIMETER LEACHINGS NOV. 11, 1949 TO NOV. 11, 1950 (58.59 INCHES RAIN DURING PERIOD)							pH OF SOILS AT END OF YEAR
	Drainage	CaCO_3 equivalent in drainage per acre	Recovery of incorporated calcium in drainage	Calcium from native soil calcium in drainage		Calculated values of native calcium based on assumed complete isotopic exchange†		
				CaCO_3 equiva- lent per acre		CaCO_3 equiva- lent per acre		
<i>Hartsells fine sandy loam</i>								
lb.	l.	lb.	per cent	lb.	per cent	lb.	per cent	
None	122.4	343	—	343	100	343	100	4.9
1000	130.7	500	25.4	246	49	275	55	5.1
2000	144.9	580	22.0	139	24	220	38	5.2
3000	137.5	794	22.3	124	16	230	29	5.4
4000	136.0	912	21.4	54	6	210	23	5.6
5000	139.9	1161	22.6	32	3	221	19	5.8
<i>Claiborne silt loam</i>								
None	143.1	288	—	288	100	288	100	5.9
1000	146.2	437	8.5	352	80	358	82	6.0
2000	147.1	615	9.5	425	69	424	69	6.2
3000	149.2	856	12.6	479	56	514	60	6.3
4000	160.0	1103	15.0	503	46	585	53	6.5
5000	152.2	1278	16.0	478	37	601	47	6.7

* All acre values calculated on the basis of 2,000,000 pounds of soil.

† Assumptions and calculations explained in text.

As noted, the soil from each of the lysimeters was analyzed for residual CaCO_3 at the end of the year. The analyses showed that there then was no residue of CaCO_3 in any lysimeter.

If it be assumed that complete isotopic exchange occurred between the calcium native to the soil and that incorporated, and that the outgo of native calcium in the drainage would be a reflection of this dilution, one could calculate the expected values for different liming rates, provided the milliequivalents of native calcium in the soil were known. From the computations given in table 2, columns 7 and 8, it will be noted that the calculated values are not in complete agreement with the experimental values.

To get some indication as to whether the amount of calcium in the soil originally had affected the trend of outgo of native calcium in the drainage, the previously described beaker-scale laboratory experiment was conducted. Hartsells soil, previously treated with 4,000 pounds of CaCO_3 per acre (table 3, column 5), showed a reversed trend of the outgo on nontagged calcium in the leachates and behaved much the same as the Claiborne soil (table 2). Although the experimental systems were not entirely comparable, the results (table 3) indicate that the amount of calcium in the soil at the beginning of the experiment influences the trend of the native calcium losses in the lysimeter drainage.

TABLE 3
*Calcium extracted from 240 gm. air-dried Hartsells fine sandy loam with
350 ml. carbonated water*

PRELIMINARY CaCO_3 INCORPORATION, PER ACRE*	LABELED CaCO_3 INCORPORATION PER ACRE	TOTAL CALCIUM IN LEACHINGS	CALCIUM FROM NONTAGGED CALCIUM IN LEACHINGS	CALCIUM FROM LABELED CALCIUM IN LEACHINGS	CALCIUM IN LEACHINGS FROM NONTAGGED	CALCULATED VALUES OF CALCIUM FROM NONTAGGED IN LEACHING†
lb.	lb.	mgm.	mgm.	mgm.	%	%
None	None	4.4	4.4	0.0	100	100
None	1000	9.2	2.2	7.0	24	55
None	2000	13.4	1.5	11.9	11	38
None	3000	20.5	1.4	19.1	7	29
None	4000	28.1	0.0	28.1	0	23
None	5000	38.0	0.0	38.0	0	19
4000	None	19.4	19.4	0.0	100	100
4000	1000	28.6	22.2	6.4	78	84
4000	2000	36.9	22.3	14.6	60	72
4000	3000	49.3	26.4	22.9	54	63
4000	4000	60.3	26.9	33.4	45	57
4000	5000	72.9	31.0	41.9	43	51

* Acre values calculated on basis of 2,000,000 pounds soil. The pH of this soil was changed from 4.7 to 5.8 by the 4,000-pound preliminary CaCO_3 incorporation.

† Calculated for dilution as explained in text.

RESULTS OF THE GREENHOUSE EXPERIMENTS

The pot cultures were in triplicate, and the values listed in table 4 are averages. The incorporation of calcium increased the crop yields (column 3), but the increase was more striking on the more acidic Hartsells soil than on the Claiborne soil, which had a better native supply of calcium. With an increase in carbonate input, the calcium content of the different crops (column 4) tended to rise. In general, the total amount of calcium removed by the crop (column 5) was increased by increasing the carbonate incorporation. This increase was not so pronounced for crops grown in the Claiborne soil. Although the values are not listed (values may be obtained by subtracting values in column 7 from those in column 5 of table 4), increasing the lime incorporation progressively increased the amount of applied calcium removed by the crops in all cases. The percentage

TABLE 4
Effect of incorporations of labeled calcium carbonate upon uptake of native and
incorporated calcium by crops grown on two soils in a greenhouse
Average values

Labeled CaCO ₃ incor- pora- tions per acre*	CROP	CROP YIELDS PER ACRE (OVEN-DRY BASIS)†	CALCIUM PER GRAM	CaCO ₃ EQUIVA- LENT IN CROPS PER ACRE†	RECOV- ERY OF INCOR- PORATED CALCIUM IN CROPS†	CALCIUM FROM NATIVE SOIL CALCIUM IN CROPS		CALCULATED VAL- UES OF NATIVE CALCIUM CALCULAT- ED FOR DILUTION‡		pH OF SOIL AFTER PLANTS GROWN
						CaCO ₃ equiva- lent per acre†		CaCO ₃ equiva- lent per acre		

Hartsells fine sandy loam—first set of crops

lb.		lb.	mgm.	lb.	per cent	lb.	per cent	lb.	per cent
None	Red clover	520	16.9	22	0	22	100	22	100
1000	Red clover	826	17.7	37	2.0	17	47	20	55
2000	Red clover	1620	19.1	77	3.0	18	23	29	38
3000	Red clover	1744	20.2	88	2.4	17	20	26	29
4000	Red clover	1801	21.5	97	2.3	5	5	22	23
5000	Red clover	1751	20.2	88	1.8	0	0	17	19
None	Rye grass	2247	5.1	29	0	29	100	29	100
1000	Rye grass	2168	6.8	37	1.7	20	55	20	55
2000	Rye grass	3144	7.8	61	2.0	21	34	23	38
3000	Rye grass	3222	8.4	68	1.7	18	26	20	29
4000	Rye grass	3026	9.6	73	1.5	14	20	17	23
5000	Rye grass	3134	9.2	72	1.2	10	15	14	19

Claiborne silt loam—first set of crops

None	Red clover	2344	16.7	98	0	98	100	98	100
1000	Red clover	2715	17.8	121	2.3	98	81	99	82
2000	Red clover	2602	18.0	117	2.0	78	67	81	69
3000	Red clover	2737	17.9	123	2.0	63	51	74	60
4000	Red clover	2420	18.6	112	1.7	47	41	59	53
None	Rye grass	3340	6.5	54	0	54	100	54	100
1000	Rye grass	3468	7.0	61	1.3	48	79	50	82
2000	Rye grass	3477	7.5	65	1.2	42	65	45	69
3000	Rye grass	3462	7.4	64	1.0	34	53	38	60
4000	Rye grass	3408	7.8	66	0.9	30	46	35	53

Hartsells fine sandy loam—second set of crops

None	Oats	1002	5.4	14	0	14	100	14	100	4.3
1000	Oats	1438	5.4	19	1.0	9	49	10	55	4.6
2000	Oats	2415	5.6	34	1.3	8	23	13	38	5.0
3000	Oats	2575	5.7	37	1.2	1	1	11	29	5.2
4000	Oats	2380	5.9	35	0.9	0	1	8	23	5.0
5000	Oats	2488	6.3	39	0.8	0	2	7	19	5.3
None	C. clover	1811	16.0	72	0	72	100	72	100	4.9
1000	C. clover	1876	19.5	91	4.1	50	55	50	55	5.0
2000	C. clover	1919	21.1	101	3.0	41	40	38	38	5.3
3000	C. clover	2009	24.0	120	3.3	20	17	35	29	5.4
4000	C. clover	2463	24.5	151	3.2	21	14	35	23	5.5
5000	C. clover	2628	25.7	169	3.0	19	11	32	19	5.6

* All acre values were calculated on basis of 2,000,000 pounds of soil.

† Values given are averages for three replications.

‡ Explained in text.

TABLE 4—Continued

LABELED CaCO ₃ INCOR- PORATIONS PER ACRE*	CROP	CROP YIELDS PER ACRE (OVEN-DRY BASIS)†	CALCIUM PER GRAM	CaCO ₃ EQUIVA- LENT IN CROPS PER ACRE†	RECOV- ERY OF INCOR- PORATED CALCIUM IN CROPS†	CALCIUM FROM NATIVE SOIL CALCIUM IN CROPS		CALCULATED VAL- UES OF NATIVE CALCIUM CALCULAT- ED FOR DILUTION‡		pH OF SOIL AFTER PLANTS GROWN
						CaCO ₃ equiva- lent per acre†		CaCO ₃ equiva- lent per acre†		
Claiborne silt loam—second set of crops										
lb.		lb.	mgm.	lb.	per cent	lb.	per cent	lb.	per cent	
None	Oats	3455	8.0	69	0	69	100	69	100	5.7
1000	Oats	3302	8.8	72	1.9	54	74	59	82	5.9
2000	Oats	3234	8.4	67	1.4	39	58	46	69	6.1
3000	Oats	3445	7.5	65	1.1	32	50	39	60	6.3
4000	Oats	3289	10.1	83	1.1	37	45	44	53	6.4
None	C. clover	2951	17.8	131	0	131	100	131	100	5.7
1000	C. clover	3021	18.5	140	2.6	114	81	115	82	6.0
2000	C. clover	2843	19.3	136	2.0	96	70	94	69	6.1
3000	C. clover	3089	20.3	157	1.8	102	65	94	60	6.4
4000	C. clover	3029	22.4	169	1.9	93	55	90	53	6.6

recovery of the added calcium through plant uptake (column 6) generally is related to increased growth, and the maximum percentage recovery is at or near the liming rate that gave maximum yields. The percentage of calcium that the crops derived from the native soil (column 8) decreased with increases in the incorporation of CaCO₃. The soils behaved differently, however, as evidenced by the fact that the highest rate of calcium input on the Hartsells caused a decrease to 15 per cent or less of native calcium, whereas that input of CaCO₃ caused a decrease to about 45 per cent on the Claiborne. The quantity of native calcium in the crops (column 7) grown on both soils decreased with increases in added calcium. This is in contrast to the results for the lysimeters (table 3, column 5), where there was a decrease in outgo from Hartsells and an increase in outgo from Claiborne.

Upon assumption of dilution of the native calcium by the incorporated calcium, the expected values of native calcium calculated for the dilutions are given in table 4, column 9, and the calculated percentage values are given in column 10. These calculated values are not in complete agreement with the values actually obtained. The ones calculated are in general larger and deviate more from the actual values with larger incorporations of CaCO₃.

DISCUSSION

The total amount of calcium removed in the drainage was much greater than that removed in the crops. Nevertheless, in general, the results of the lysimeter and greenhouse experiments are of similar import.

Borland and Reitemeier (1) obtained complete isotopic exchange of Ca45 in a short time in the system they studied, but their system is not comparable to that used in these experiments. The review of Giesecking (3) points out that as

the amount of exchangeable calcium on the clay mineral crystals becomes less, the calcium becomes more and more difficult to release. Marshall (8) discussed the fact that the calcium of clay possesses a range of activity. If there were complete isotopic exchange between the native calcium and additive calcium, one would expect the calculated values, based on dilution, to be in accord with the ones actually obtained. This was not the case, particularly for the Hartsells soil at high rates of CaCO_3 incorporation. One might postulate that the discrepancy between the actual and calculated values might be attributed in some way to such factors as (a) unreacted labeled CaCO_3 , (b) incomplete isotopic equilibrium between Ca^{45} and native soil calcium, (c) eluviation of solid CaCO_3 particles, and (d) experimental error.

As previously indicated, when the soil from each lysimeter was analyzed for unreacted CaCO_3 at the end of the experiment, none was found. The speed of the reaction of the CaCO_3 with the soil would depend upon factors such as fineness of material, thoroughness of mixing with the soil, amount of calcium already in the soil, and moisture relations. It is not known how quickly the reaction took place, but the long experience of some of the authors with lime problems makes the writers feel that the reaction of the CaCO_3 with the soil was relatively rapid.

When a treatment is applied to a colloid, it is not uncommon for the reaction to occur slowly and equilibrium to be delayed. It is conceivable that equilibrium between the Ca^{45} and the native soil calcium had not been reached. This postulation, however, does not seem to be in harmony with what was pointed out in the presentation of results; namely, the percentages of calcium from the native soil calcium in the first set of samples were similar to those of the ninth set, obtained at the end of a year. If isotopic exchange were continuing, the rate was so slow it was not discernible over a year's time.

In lysimeter experiments dispersed particles may occur when the leachates carry a low content of solutes. Such an occurrence was not observed in the present experiments, and therefore it is most improbable that some labeled CaCO_3 solid particles passed out in the drainage. What effect would such an improbability have in connection with the analysis on the proportion of native to labeled calcium? If the particles of CaCO_3 did not get in the drainage sample to be analyzed, obviously they would have no effect; if they did get in the drainage samples the acid used in the analytical procedure would dissolve them, and the results would be high for labeled calcium. This would increase the ratio of labeled calcium to native calcium, and this effect should be more pronounced in the first leaching when unreacted CaCO_3 may still have been present. It was pointed out, however, that the percentages were relatively constant for the nine sets of leachings.

The experimental error cannot be estimated, but it is thought to be small. In every case the calculated values for native calcium from the Hartsells soil are higher than the actual values except, of course, from the lysimeter that received no CaCO_3 . Because of their similarity, the nine sets of values for the samples of drainage water at different periods are given only as totals.

Upon this reasoning the authors conclude that isotopic exchange between the Ca^{45} and the native soil calcium was not complete.

It is difficult to postulate a mechanism that would explain all the observed facts. The additive calcium increased the outgo of native calcium in the drainage from the Claiborne soil, the soil of higher content of exchangeable calcium, but decreased such outgo progressively in the drainage from the Hartsells. One might suppose that differences in the secondary clay minerals of the two soils would have something to do with this. There may be differences, but Pearson and Ensminger (9) showed that the clay separates from the Hartsells and the Decatur series, which is closely related to the Claiborne, were both kaolinitic. A review of the literature indicates that not all the exchangeable calcium of the soil is held with equal force and that this difference in attraction for the calcium probably is a factor. Dilution would account, in part, for the trends observed. In a laboratory experiment on the Hartsells soil, the trend of the loss of untagged calcium in the leachate was reversed through a prior increase in calcium supply in the soil. Hence it appears that there is something about the calcium supply of the soil, or the pH, or both, that affects the soil system and governs the amount of native calcium that goes out in the drainage.

The study of these problems is being continued.

SUMMARY

Labeled calcium carbonate was incorporated at several rates in Hartsells fine sandy loam and in Claiborne silt loam, and conventional lysimeter and greenhouse experiments were conducted to determine the migrations of native calcium and applied calcium in the rain water drainage and in the crops grown on the same soils in pot cultures.

The findings of the lysimeter and greenhouse experiments were similar in general. Increasing the calcium incorporations caused increases in the leachings of total calcium and additive calcium in the lysimeter and crop experiments. Isotopic exchange between Ca^{45} and the native soil calcium did not appear to be complete.

The additive calcium increased the quantity of native calcium in the drainage from Claiborne soil but decreased it progressively in the drainage from the Hartsells soil.

In a laboratory experiment performed on the Hartsells soil, the trend of the results was reversed through a build-up of the soil's supply of calcium prior to the introduction of labeled calcium carbonate. This soil was thus made to behave somewhat like the Claiborne.

REFERENCES

- (1) BORLAND, J. W., AND REITEMEIER, R. F. 1950 Kinetic exchange studies on clays with radioactive calcium. *Soil Sci.* 69: 251-260.
- (2) COMAR, C. L., ET AL. 1951 Use of calcium⁴⁵ in biological studies. *Nucleonics* 8: 19-31.
- (3) GIESEKING, J. E. 1949 Clay minerals in soils. *Advances in Agron.* 1: 159-204.
- (4) HARRIS, H. C., ET AL. 1951 Radioactive calcium in the study of additive and native supplies in the soil. *Science* 113: 328-329.
- (5) MACINTIRE, W. H. 1926 Influence of form, soil-zone, and fineness of lime and magnesia incorporations upon outgo of calcium and magnesium. *Soil Sci.* 21: 377-391.
- (6) MACINTIRE, W. H. 1926 Reciprocal repression by calcic and magnesian additions to surface soil. *Jour. Amer. Soc. Agron.* 18: 482-497.

- (7) MACINTIRE, W. H., AND WINTERBERG, S. H. 1946 Pot method for soil cultures. *Soil Sci.* 62: 33-41.
- (8) MARSHALL, C. E. 1948 Ionization of calcium from soil colloids and its bearing on soil-plant relationships. *Soil Sci.* 65: 57-68.
- (9) PEARSON, R. W., AND ENSMINGER, L. E. 1949 Types of clay minerals in Alabama soils. *Soil Sci. Soc. Amer. Proc.* (1948) 13: 153-156.
- (10) SHAW, W. M., MACINTIRE, W. H., AND HILL, H. H. 1949 Conservation of calcium and magnesium from inputs of burnt lime, limestone, dolomite, and dicalcium silicate, as influenced by rate and frequency of liming and by zone of incorporation. *Tenn. Agr. Exp. Sta. Bul.* 212.
- (11) WALKLEY, A., AND BLACK, I. A. 1934 An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* 37: 29-38.

RADIATION EFFECTS ON PLANTS GROWN IN SOIL TREATED WITH FERTILIZER CONTAINING P32

JAMES M. BLUME

*U. S. Department of Agriculture*¹

Received for publication August 29, 1951

Use of radioisotopes in plant nutrition experiments is justifiable only when it can be shown that the radiation to which the plant is exposed during the experiment has no appreciable effect upon the growth and ion intake of the plant. The results obtained by the various workers who have investigated this problem are not entirely consistent. Russell and Martin (7) reported damage to the roots of young barley plants grown in nutrient solutions containing very low levels of P32. Blume *et al.* (1) found that under the conditions of their experiments considerably higher specific activity levels of P32 in the culture media were necessary to cause measurable effects upon leaf lengths or upon dry weights of shoots or roots of young barley plants grown in solutions. Histological examinations of the growing regions of these plants indicated, however, that even the smallest amounts of radiation were sufficient to affect the size of meristematic cells of the shoot (6). No effect of specific activity level upon phosphorus uptake was found.

In soil culture experiments, Dion *et al.* (3) and Hendricks and Dean (4) showed that yields of cereal tops were not affected by P32 specific activities considerably higher than those ordinarily used in field or greenhouse work. Russell *et al.* (8) found, however, that the ratio of fertilizer phosphorus to soil phosphorus in the plant might be significantly altered by changing the P32 level of the fertilizer, even though there was no effect upon the weights of tops. Bould *et al.* (2) found both dry weights of tops of barley plants and the ratio of fertilizer phosphorus to soil phosphorus were sometimes affected at rather low P32 levels, but pointed out the low magnitudes of the radiation effects, even when comparatively high specific activity levels of P32 were used.

EXPERIMENTAL METHODS

The work reported here deals with two experiments in which cereals grown in the greenhouse were fertilized with KH_2PO_4 solutions of several ratios of P32 to P31. In each experiment, the soil was fertilized in bulk with 75 pounds N and 150 pounds K_2O per acre, the sources being NH_4NO_3 and KCl. The soil was then weighed into No. 10 cans, brought up to moisture, and planted, after which the proper phosphate solutions were added to the surface of the soil as a coarse spray at the rate of 200 ml. solution per can and 50 pounds P per acre. This method of application caused retention of all of the labeled phosphate in the top inch or two of soil. The P32 used in the experiments was the

¹ Bureau of Plant Industry. This investigation was supported in part by the U. S. Atomic Energy Commission. The author is indebted to E. C. Simpson, Jr., for the plant analyses reported.

separated isotope prepared by pile irradiation of sulfur and listed in the catalog of the Isotopes Division of the Atomic Energy Commission as Item S-3.

In the first experiment, 14 seeds of barley were planted in each 8-pound can of Evesboro sand. KH_2PO_4 solutions containing 0, 20, 100, 500, 2,500, and 12,500 microcuries P32 per gram P were then added. The seedlings were thinned to 10 per can 5 days after planting. Of the 12 replicates, 6 were harvested 33 days after planting and the remaining 6 were harvested at the end of 54 days.

In the second experiment, oats were grown on Chester loam. Each of 60 cans received $7\frac{1}{2}$ pounds of this soil, which had been fertilized with N and K_2O as previously described. In another series of 36 cans, $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at the rate of 100 pounds P per acre was mixed with 5 pounds of fertilized soil and the mixture placed in the bottoms of the cans. The remaining $2\frac{1}{2}$ pounds of soil required to fill each can received no calcium phosphate. This "added phosphate" series was introduced into the experiment to provide the plants a source of highly available phosphorus as an alternative to the labeled phosphate application.

All of the filled cans were brought up to moisture, allowed to incubate for 12 days, and planted with 20 seeds per can. KH_2PO_4 solutions containing 10, 50, 250, 1,250 and 6,250 microcuries P32 per gram P31 were added to the cans that had received no previous phosphate; solutions containing 10, 250, and 6,250 microcuries P32 per gram P31 were added to the "added phosphate" series. Each treatment was replicated 12 times. The seedlings were thinned to 15 per pot 9 days after planting. Half of the replicates were harvested 21 days after planting, and the other half were harvested at the end of 43 days.

In both experiments, the harvested tops were dried at 70°C ., weighed, ashed, analyzed for total phosphorus, and counted for P32. Total phosphorus was determined colorimetrically by the molybdovanadate method, and P32 counts were made on ammonium magnesium phosphate precipitates collected on filter disks according to the method of MacKenzie and Dean (5). Total phosphorus determinations and P32 counts on portions of each of the fertilizing solutions were made by the same methods as those used for the plant materials, and served as standards for the calculation of the percentage of plant phosphorus derived from the fertilizer.

RESULTS

The dry weights and the percentages of plant phosphorus derived from the fertilizer solutions for the barley grown on the Evesboro soil are given in table 1. Similar data for the two series in which oats were grown on the Chester soil are given in tables 2 and 3. All results shown in the three tables are averages of six replications.

In the experiment with barley grown on the Evesboro soil, a significant decrease in dry weight of tops was caused by the highest ratio of P32 to P31 tried, but none of the lower specific activities caused yields significantly different from those of the control. The percentage of total phosphorus in the tops followed the same pattern as the yields, only the very highest specific activity treatments differing

significantly from the controls. The fraction of the plant phosphorus originating from the fertilizer solution was not significantly affected by the specific activity of the fertilizer at the time of the first harvest. At the second harvest, the percentage of the phosphorus in the tops derived from the fertilizer appeared to be

TABLE 1

Dry weight and phosphorus content derived from fertilizer for barley grown on Evesboro sand

P32 TREATMENT PER GM.P	HARVESTED 33 DAYS			HARVESTED 54 DAYS		
	Dry wt. of tops	P content of tops		Dry wt. of tops	P content of tops	
		Total	From fertilizer		Total	From fertilizer
$\mu\text{C.}$	gm.	per cent	per cent	gm.	per cent	per cent
0	3.58	0.42	—	6.34	0.30	—
20	3.63	0.42	80.76	6.17	0.30	83.64
100	3.62	0.39	79.99	6.52	0.29	78.44
500	3.59	0.45	77.84	6.05	0.30	80.26
2,500	3.53	0.41	79.62	6.55	0.30	79.98
12,500	3.16	0.50	77.48	5.53	0.37	76.08
L.S.D. (5%).....	0.21	0.02	n.s.	0.37	0.02	1.63
L.S.D. (1%).....	0.29	0.03	—	0.50	0.02	2.22

TABLE 2

Dry weight and phosphorus content derived from fertilizer for oats grown on Chester loam

P32 TREATMENT PER GM.P	HARVESTED 21 DAYS			HARVESTED 42 DAYS		
	Dry wt. of tops	P content of tops		Dry wt. of tops	P content of tops	
		Total	From fertilizer		Total	From fertilizer
$\mu\text{C.}$	gm.	per cent	per cent	gm.	per cent	per cent
10	0.90	0.39	67.08	9.16	0.20	79.78
50	0.93	0.38	67.34	9.03	0.20	81.86
250	0.95	0.39	66.77	9.09	0.20	81.11
1,250	0.81	0.40	65.14	9.09	0.20	79.09
6,250	0.82	0.38	60.32	8.17	0.22	79.64
L.S.D. (5%).....	0.10	n.s.	3.12	0.45	n.s.	1.56
L.S.D. (1%).....	—	—	4.26	0.60	—	—

significantly higher at the level of 20 microcuries per gram than at any of the higher activities. Plants grown at the levels of 100, 500, and 2,500 microcuries per gram did not vary significantly from one another, but plants grown with fertilizer containing 12,500 microcuries P32 per gram phosphorus showed the fertilizer-derived fraction of their phosphorus to be significantly lower than for any of the other treatments.

In the second experiment, the yields and the total phosphorus content of the

tops were either affected not at all, or were affected only at the highest specific activity level, 6,250 microcuries of P32 per gram of P31. This was true of both harvests on each series.

At the first harvest of the series in which no additional phosphate had been added to the soil in the bottom two-thirds of the cans, only the plants grown with 6,250 microcuries P32 per gram P31 differed significantly from the others in percentage of plant phosphorus derived from the fertilizer. At the second harvest of this series, the 10-, 1,250-, and 6,250-microcurie treatments all appeared to have significantly smaller fractions of their plant phosphorus from the fertilizer than the 50- and 250-microcurie levels. The plants grown on the series in which the soil in the lower two-thirds of the can received additional phosphate showed no significant differences at either harvest in the fraction of plant phosphorus derived from the fertilizer.

TABLE 3

Dry weight and phosphorus content derived from fertilizer for oats grown on Chester loam fertilized with unlabeled monocalcium phosphate in lower two-thirds of pot

P32 TREATMENT PER GM.P	HARVESTED 21 DAYS			HARVESTED 42 DAYS		
	Dry wt. of tops	P content of tops		Dry wt. of tops	P content of tops	
		Total	From fertilizer		Total	From fertilizer
		per cent	per cent		per cent	per cent
$\mu\text{c.}$	<i>gm.</i>			<i>gm.</i>		
10	1.12	0.53	26.15	9.10	0.31	38.22
250	1.16	0.51	24.78	9.56	0.32	35.73
6,250	1.06	0.47	24.21	8.76	0.35	34.20
L.S.D. (5%).....	n.s.	0.04	n.s.	0.49	0.02	n.s.

DISCUSSION

The outstanding characteristic of these results is the smallness of the variations in yield, phosphorus content, and percentage of phosphorus derived from the fertilizer associated with change in P32 application. Only by the last of these criteria have statistically significant differences been shown at moderate levels of activity. Since the differences often failed to follow a consistent trend throughout the range of treatments studied, and because of the difficulty found by others in reproducing the results from this type of experiment, some doubt as to the direct connection between these differences and radiation injury may be pardonable, except at very high levels of P32 application.

As has been mentioned, the soil in the lower part of the pots of one series of the second experiment received a heavy application of unlabeled monocalcium phosphate, thus providing the plant a source of highly available phosphorus as an alternative to the labeled fertilizer added to the surface. The thought was that radiation injury might be more strongly reflected by the percentage phosphorus derived from the fertilizer under these conditions than when the only

option open to the plant was between the radioactive phosphorus added in solution and the rather unavailable soil phosphorus. No such effect was found. Though a consistent decrease in the percentage of the plant phosphorus derived from the fertilizer was found to be associated with increasing specific activity of the fertilizer solution in this particular series, it was too small to be statistically significant.

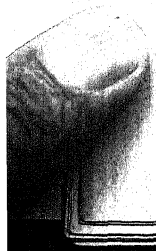
In these experiments, the effects of radiation from P32 upon plant growth and intake of phosphorus have been so small as to be unimportant from a practical standpoint. Certainly none of them have been great enough to preclude the use of radiophosphorus in reasonable concentrations in fertilizer experiments. Because of plant cell changes that have been shown by other types of experiment (6) to be associated with small doses of radiation, however, the researcher who uses radioisotopes in plant experiments is well advised to consider the possibility of radiation injury when designing experiments.

SUMMARY

Experiments were carried out with barley and oats grown in the greenhouse on soils that had received surface applications of KH_2PO_4 solutions containing 0 to 12,500 microcuries P32 per gram of P31. Over this range, which includes concentrations much higher than those usually used in plant nutrition studies, differences in dry weight of tops, phosphorus content of tops, and percentage of phosphorus in the tops derived from the fertilizer were, although sometimes statistically significant, too small appreciably to affect the data gained by the use of the isotope.

REFERENCES

- (1) BLUME, J. M., HAGEN, C. E., AND MACKIE, R. W. 1950 Radiation injury to plants grown in solutions containing P32. *Soil Sci.* 70: 415-426.
- (2) BOULD, C., NICHOLAS, D. J. D., AND THOMAS, W. D. E. 1951 Radiation effects in plant nutrition experiments with phosphorus-32. *Nature* 167: 140-142.
- (3) DION, G., ET AL. 1949 Plant injury from phosphorus-32. *Nature* 163: 906-907.
- (4) HENDRICKS, S. B., AND DEAN, L. A. 1948 Basic concepts of soil and fertilizer studies with radioactive phosphorus. *Soil Sci. Soc. Amer. Proc.* (1947) 12: 98-100.
- (5) MACKENZIE, A. J., AND DEAN, L. A. 1948 Procedure for measurement of P31 and P32 in plant material. *Analyt. Chem.* 20: 559-560.
- (6) MACKIE, R. W., BLUME, J. M., AND HAGEN, C. E. Histological changes induced in barley plants by radiation from P32. *Amer. Jour. Bot.* (in press).
- (7) RUSSELL, R. S., AND MARTIN, R. P. 1949 Use of radioactive phosphorus in plant nutritional studies. *Nature* 163: 71-72.
- (8) RUSSELL, R. S., ADAMS, S. N., AND MARTIN, R. P. 1949 Radiation effects due to phosphorus-32 in fertilizer experiments. *Nature* 164: 993-995.



UPTAKE AND MOVEMENT OF FERTILIZER PHOSPHORUS

J. JORDAN, C. SIMKINS, G. COREY, R. KNIGHT, AND G. O. BAKER

Idaho Agricultural Experiment Station¹

Received for publication June 11, 1951

Since the introduction of radioisotopes to agricultural research, investigators have confined their efforts mainly to fertilizer type and placement studies. Though much remains to be done in this type of work, efforts are now being diverted to other fields of investigation. For example, investigators want to know the effect of soil moisture on the availability of plant nutrients and on the movement of these nutrients in the soil.

Various workers have studied the mobility of phosphorus in soils and have reported conflicting results. Few have studied the influence of moisture tension on availability of phosphorus. Russell (8) wrote that phosphates do not naturally move readily in a soil, and to enrich the subsoil or root zone with phosphorus, the phosphate must be worked directly into the subsoil. Midgley (6) found that superphosphate applied as a surface dressing moves downward very slowly. In his trials, most of the phosphate was found to be in the surface 1 inch of soil even after 6 months. On the other hand, Stephenson and Chapman (10) reported that fertilizer phosphate penetrated a foot below the surface in light to medium textured soils; there was little or no penetration in heavy soils. Waynick and Leavitt (12), who added phosphate fertilizer to the soils in irrigation water, reported the fixation of phosphoric acid in the upper 4 inches of heavy soil types. They recommended three applications of fertilizer, one in fall and two in early spring, to allow the phosphoric acid to penetrate to a depth of 2 feet. These authors, and Neller (7) indicated that increasing the amounts of water applied causes the phosphorus to penetrate deeper into the soil.

The objectives in this experiment were (a) to determine the effect of moisture tension upon phosphorus uptake by potatoes from banded and broadcast superphosphate at various stages of growth; (b) to measure the proportion and total uptake of phosphorus supplied by the fertilizer and by the soil; (c) to study fertilizer phosphorus movement in the soil as influenced by applications of 1, 3, and 7.5 inches of water at each irrigation.

MATERIALS AND METHODS

Field study

The experiment was conducted on Declo fine sandy loam at the Aberdeen Agricultural Experiment Station in Southwestern Idaho. Analysis of the soil was as follows: pH (surface 8 inches), 7.8; available P_2O_5 , 6 to 20 ppm.; total nitrogen, 0.08 to 0.09 per cent; total soluble salts, 945 ppm.; $CaCO_3$, 1.0 per

¹ Idaho Agricultural Experiment Station Research Paper No. 335. Radioactive superphosphate for this experiment supplied by the U. S. Department of Agriculture, Beltsville, Maryland.

cent; field capacity, 15.8 per cent. The experimental site received a blanket application of 20 pounds of nitrogen per acre as $(\text{NH}_4)_2\text{SO}_4$ before planting of certified Idaho Russet potatoes on May 15, 1950.

The phosphate carrier used in the study was single superphosphate analyzing 18.5 per cent P_2O_5 . A part of the phosphate was tagged with P32, which had an activity of about 0.2 millicuries per gram of P_2O_5 at planting time. Two methods of application were used: first, the fertilizer at a rate of 40 pounds P_2O_5 per acre, was banded 4 inches to one side of the seed piece and 4 inches deep; second, the fertilizer, at rates of 40 and 80 pounds P_2O_5 per acre, was broadcast on the surface and disked into the soil to a depth of 4 or 5 inches.

Low and high moisture tension levels for each treatment were studied. Composite soil moisture samples were taken from each plot prior to each irrigation, and moisture was determined by oven-drying. The soil moisture values were averaged for each irrigation date for the different moisture levels.

The plots were irrigated by the corrugation method. The irrigation period was 8 hours, and approximately 3 acre-inches of water was applied at each irrigation. The low moisture tension plots received about 30 acre-inches of water, and the high moisture tension plots, about 15 acre-inches of water during the irrigation season.

The soil moisture values were converted to tension values from a moisture retention curve supplied by the U. S. Regional Salinity Laboratory. The soil moisture tensions from July 6, when the moisture treatments began, to September 8 averaged 955 and 1,222 cm. of water for the low and high tensions, respectively.

A split plot design was used. The four fertilizer treatments—check, 40 pounds P_2O_5 per acre banded, 40 and 80 pounds P_2O_5 per acre broadcast—were randomized. The moisture treatments were not randomized, since the water flowed the length of the field to facilitate irrigation. Each treatment was replicated six times.

Eight rows of potatoes were grown per subplot. Only the third row of potatoes was treated with the tagged superphosphate.

Leaf samples for analysis were collected from each hill of rows fertilized with tagged P_2O_5 (a) when the plants were 4 to 5 inches high, June 26; (b) at early bloom, July 23; (c) before leaves began falling, August 22; and (d) at harvest time, October 2. At the third and fourth sampling dates tubers were harvested from the tagged P_2O_5 rows. These samples were all analyzed for total phosphorus and P32. Also at the third and fourth periods two of the regular phosphated rows were harvested for yield. Vines were harvested at the third sampling date only.

Available soil P_2O_5 was determined by the CO_2 -extraction method (1). Leaf and tuber samples were dried and ground prior to analysis. Phosphorus 32 activity was determined by the briquette method (4), except for the final tuber samples, which were digested and the P_2O_5 precipitated on filter rings as magnesium ammonium phosphate hexahydrate (3). Plant P_2O_5 was determined by the vanadomolybdate method (2).

Greenhouse study

To determine the influence of the amount of irrigation water on movement of P32 in the soil in the greenhouse, surface soil to a depth of 6 inches was taken from the field where the potato experiment was conducted. It was air-dried, sieved, thoroughly mixed, and placed in steel cylinders, 15 inches long, which had been painted on the inside with Biturine paint. Each cylinder received 9 kgm. soil. To minimize channeling when water was added, the soil was carefully tamped with a 3.5-kgm. tamper while being loaded.

Superphosphate tagged with P32 was applied to the surface at a rate of 80 pounds P_2O_5 per acre. To facilitate even distribution, 10 gm. of finely sieved soil was mixed with the phosphate before application. The cylinders were placed on metal trays so the drainage water could be collected for radioactivity testing and disposal.

Water of the same composition as that used in the field experiment was applied at rates of 1, 3, and 7.5 inches per irrigation. Each irrigation treatment was replicated six times.

The soil was sampled 6 weeks after the fertilizer was applied and after it had received two irrigations made 2 weeks apart. The soil, still moist, was removed from the cylinders with little disturbance to the columns. Soil sections were sliced off at $\frac{1}{2}$, 1, 2, 3, and 4 inches below the surface. These were air-dried, sieved, and thoroughly mixed. From each sample, 5 gm. was made into a briquette for determination of radioactivity.

Radioautographs² of 5-inch cores from the different treatments were made. The cores were wrapped in waterproof plastic to prevent spoilage of the film by moisture.

RESULTS AND DISCUSSION

Phosphorus in plant leaf

The percentage of fertilizer phosphorus in the plant leaf, that is, the plant uptake from the applied fertilizer, was influenced very markedly by fertilizer treatment, sampling date, and soil moisture tension. Table 1 shows that the 40-pound broadcast treatment provided significantly more fertilizer phosphorus than did the 40-pound band treatment. As might be expected, the 80-pound broadcast treatment furnished an even greater amount of fertilizer phosphorus.

Percentage uptake of fertilizer phosphorus by the plant leaf was highest at the first sampling date, 42 days after planting. Spinks and Barber (9) have also reported early utilization of fertilizer phosphorus. They found that virtually all the phosphorus taken up by the fertilized young plant came from the fertilizer. As shown in table 1, percentages of fertilizer phosphorus in the plant leaf decreased significantly as the growing season progressed.

The effect of soil moisture tension on the plant uptake of fertilizer phosphorus

² Technique developed by C. E. Michelson, Physical Sciences Department, University of Idaho.

is shown in table 1. On the average there was significantly more fertilizer phosphorus in the leaves of all plants grown on the low soil moisture tension plots than in leaves of plants grown on the high tension plots, irrespective of method or rate of application or of sampling date. The low tension plots received about twice as much water during the season as did the high tension plots.

There was an interaction of fertilizer treatment and sampling date, as indicated in table 2. Based on percentage fertilizer phosphorus content of leaves at the first sampling, there is an indication that the 40-pound band treatment furnished more fertilizer phosphorus than did the 40-pound broadcast treatment. At the following two sampling dates the broadcast treatment furnished significantly more fertilizer phosphorus than did the band treatment. The 80-pound broadcast treatment supplied significantly more fertilizer phosphorus than did either of the other two treatments at the first sampling date.

TABLE 1

Influence of rate and placement, stage of growth, and soil moisture tension on average percentage of phosphorus content of potato leaves and tubers supplied by fertilizer

	P FROM FERTILIZER							
	Fertilizer treatment			Days after planting			Soil moisture tension	
	40 lb./A. band	40 lb./A. broadcast	80 lb./A. broadcast	42	69	99	High	Low
	%	%	%	%	%	%	%	%
Leaves.....	3.84	4.58	7.07	7.08	5.63	2.77	4.68	5.64
LSD.....	1 per cent—0.67			1 per cent—0.88			5 per cent—0.82	
Tubers.....	2.00	2.98	4.90	Ave. value 3.3			3.00	3.80
LSD.....	5 per cent—0.80			—			5 per cent—0.70	

There was an interaction between soil moisture tension and sampling date (table 2). There was no difference in the percentage fertilizer phosphorus content of the leaves at the first sampling date. This was expected, since spring rains prevented maintenance of soil moisture differences during the first 50 days after planting. At the second sampling date, 19 days after moisture control became possible, there was a significantly greater percentage of fertilizer phosphorus in the leaves from plants on the low tension plots than in the leaves of plants on the high tension plots. At the third sampling date this difference was not significant.

Uptake of fertilizer P by tubers

The fertilizer P content of the immature tubers sampled 99 days after planting and that of the mature tubers sampled 142 days after planting were significantly higher on the 40-pound broadcast treatment than on the 40-pound band treatment (table 1). The tubers, whether immature or mature, derived signifi-

cantly more phosphorus from the fertilizer at the lower soil moisture tension than when at the higher tension (table 1).

The results for the tubers closely parallel the results for the leaves with one exception: in the tubers, there was no significant difference between their per-

TABLE 2
Effect of fertilizer treatment and soil moisture tension on the uptake of P_2O_5 from fertilizer by leaves

TREATMENT	P IN LEAF FROM FERTILIZER		
	Days after planting		
	42	69	99
	%	%	%
40 lb. band.....	6.15	3.78	1.57
40 lb. broadcast.....	5.62	5.39	2.72
80 lb. broadcast.....	9.47	7.72	4.03
LSD.....	1 per cent—2.15; 5 per cent—1.62		
Soil moisture tension			
High.....	6.99	4.69	2.37
Low.....	7.17	6.57	3.18
LSD.....	1 per cent—1.76; 5 per cent—1.32		

TABLE 3
Influence of fertilizer treatments and soil moisture on phosphorus uptake by tubers from fertilizer
 P_2O_5 from fertilizer

DAYS AFTER PLANTING	FERTILIZER TREATMENT			SOIL MOISTURE TENSION	
	40 lb./A. band	40 lb./A. broadcast	80 lb./A. broadcast	High	Low
	lb./A.	lb./A.	lb./A.	lb./A.	lb./A.
99	0.12	0.21	0.34	0.20	0.26
LSD.....	1 per cent—0.08			5 per cent—0.05	
142	1.90	2.59	4.67	2.45	3.66
LSD.....	5 per cent—1.49			5 per cent—1.05	

centage fertilizer phosphorus content at the two sampling dates. The yield of tubers at the second sampling date was much higher than that at the first sampling date, and therefore the weight of fertilizer phosphorus in the tubers was more than 10 times as great at the second sampling date, as shown in table 3. A similar relationship is shown in table 3 between the weights of fertilizer phosphorus recovered by tubers from the two soil moisture tension treatments.

The 40-pound broadcast treatment had furnished significantly more fertilizer phosphorus to the tubers by the first sampling date than had the 40-pound band treatment. At harvest, the difference was not significant even at the 10 per cent level.

There was a significant interaction between fertilizer treatment and soil moisture tension at the final sampling date, as shown in table 4. At harvest time the soil moisture tension had considerably more influence on the fertilizer phosphorus uptake at the 80-pound rate than it did at either of the 40-pound rates.

TABLE 4

Total uptake of fertilizer P_2O_5 by tubers at harvest time as influenced by fertilizer treatments and soil moisture tension
 P_2O_5 from fertilizer

SOIL MOISTURE TENSION	FERTILIZER TREATMENT		
	40 lb./A. band	40 lb./A. bdcst.	80 lb./A. bdcst.
	lb./A.	lb./A.	lb./A.
High.....	1.52	2.28	3.55
Low.....	2.28	2.90	5.80
LSD.....	10 per cent—1.02; 5 per cent—1.25		

TABLE 5

Total uptake of soil P_2O_5 by tubers at harvest time as influenced by fertilizer treatments and soil moisture tension
 Soil P_2O_5

FERTILIZER TREATMENT				SOIL MOISTURE TENSION	
CHECK	40 lb./A. band	40 lb./A. broadcast	80 lb./A. broadcast	High	Low
lb./A.	lb./A.	lb./A.	lb./A.	lb./A.	lb./A.
8.53	18.52	25.21	44.0	19.87	28.25
LSD.....	5 per cent—10.05; 1 per cent—13.90			5 per cent—7.61	

Uptake of soil P_2O_5 by tubers

At harvest time there was significantly more soil P_2O_5 in the tubers grown on the phosphated plots than in tubers on the untreated plots, as shown in table 5. Spinks and Barber (9) reported that wheat took up more soil phosphorus from phosphated treatment than from check plots. Strzemienski (11) reported similar results with rye grass. The difference between uptake of soil P_2O_5 on the check plots and that on the plots receiving the 40-pound band treatment was significant only at the 10 per cent level. The difference in uptake of soil P_2O_5 by tubers on the check plots and on the 40-pound broadcast plots, however, was highly significant. Similar results have been obtained in an investigation³ of availability

³ Unpublished data, Agricultural Chemistry Department, University of Idaho.

of fertilizer P_2O_5 under varying soil conditions. These have shown that more soil P_2O_5 is available on phosphated soil than on soil receiving no phosphate.

Yields of vines and tubers

Vines of plants were cut for yield when the leaves were sampled 99 days after planting. Despite the difference in fertilizer phosphorus values in the leaves at this sampling green vine weights showed no significant differences due to fertilizer treatments or soil moisture tension, nor was there any interaction of these two variables. The over-all average from all treatments was about 5.5 tons of green vines per acre.

Tubers harvested at the same time as the vines showed that no significant differences in yields due to the fertilizer treatments or to the two moisture levels. There was no interaction between these two variables. The over-all average yield from all treatments was about 7.2 tons per acre.

TABLE 6

Influence of amount of irrigation water on downward movement of superphosphate tagged with P_{32}

TOTAL IRRIGATION WATER APPLIED	MEAN COUNTS PER SECOND AT INCREASING SOIL DEPTHS				RADIOAUTOGRAPHS— DEPTH OF OBSERVED PENETRATION
	0-½ inch	½-1 inch	1-2 inches	2-4 inches	
<i>inch</i>					<i>inch</i>
2	3.90	2.05	0.60	tr.	0.5
6	2.79	2.17	1.63	tr.	1.0
15	1.94	1.79	1.84	0.51	3.0
LSD.....	Depths × levels— 1 per cent—0.72; Two depths at one level or 2 levels at one depth—1 per cent—0.93				—

Tubers at the final harvest showed no significant differences in yields between treatments. The average yield from all treatments was about 10 tons per acre. These tubers were graded, and the yields of No. 1, No. 2, and cull grades were determined. None of these data showed significant differences in weight between the various treatments within the three grades. The lack of yield response despite the increased amounts of P_2O_5 taken up by the tubers grown on the fertilized plots requires some explanation. Macy (5) related nutrient concentration and yield response of plants to three zones of nutrition. His zone of "luxury consumption" applies here. Since soil nitrogen in the experimental field was low, approximately 0.08 per cent, this deficiency resulted in a "luxury consumption" of phosphorus without increased growth.

Movement of fertilizer phosphorus in soil

That the phosphorus from superphosphate was moved downward into the soil by irrigation water under the conditions studied is shown in table 6. This helps explain the excellent results being obtained from broadcast application of phosphate fertilizer to legumes in the irrigated sections of southern Idaho.

The data shows that a total of 2 inches of irrigation water moved the fertilizer phosphorus from the surface into the first inch of soil, and 6 inches of irrigation water moved the fertilizer phosphorus into the second inch of soil. The 6-inch irrigation moved significantly more fertilizer phosphorus from the surface than did the 2-inch irrigation. Significantly more fertilizer phosphorus was moved from the top $\frac{1}{2}$ inch by the 15-inch total irrigation than by the smaller irrigation rates. It also went deeper and was more evenly distributed.

Drainage water from the cylinders was collected for P32 determinations. There was no drainage from the cylinders receiving only 2 inches of irrigation water. There was a trace of P32 activity in the drainage water from the 6- and 15-inch treatments.

These data were further substantiated by radioautographs of the soil cores taken from the three treatments. The average length of film exposed by P32 in the applied fertilizer, showing depth of penetration under the three irrigation treatments, is also shown in table 6.

Errors due to channeling were undoubtedly small, since there was no evidence of significant difference between replications in the activity measurements above 4 inches and activities were negligible below 4 inches. Furthermore, the significant differences between treatments indicates that channeling can be discounted as a serious source of error.

CONCLUSIONS

Band application provided more fertilizer phosphorus for plant use in the earliest stages of growth than did broadcast application. When plants were 6 to 12 inches high, the broadcast treatment was supplying more fertilizer phosphorus than the band treatment. Results indicate that placement of phosphate fertilizer is not necessary for crop utilization under the conditions of the experiment.

Soil moisture tension exerts a considerable influence on the phosphorus uptake by potatoes from the fertilizer applied and from the soil. The potatoes took up more fertilizer and soil phosphorus at the low soil moisture tension than at the high tension.

Plants were able to absorb more soil phosphorus from soil treated with superphosphate than from untreated soil.

Tubers grown under low soil moisture tension conditions recovered only 6 per cent of the fertilizer P as P_2O_5 when the fertilizer was banded at 40 pounds per acre and 7 per cent when the fertilizer was broadcast at 40- and 80-pound rates.

The amount of irrigation influences the downward movement of fertilizer phosphorus in the soil. The greater the amount of water, the greater the downward movement of fertilizer phosphorus.

REFERENCES

- (1) ENSMINGER, L. E., AND LARSON, H. W. E. 1944 Carbonic acid soluble phosphorus and lime content of Idaho soils in relation to crop response to phosphate fertilization. *Soil Sci.* 58: 253-258.
- (2) KITSON, R. E., AND MELLON, M. G. 1944 Colorimetric determination of phosphorus

- as molybdivanadophosphoric acid. *Indus. and Engin. Chem., Analyt. Ed.* 16: 379-383.
- (3) MacKENZIE, A. J., AND DEAN, L. A. 1948 Procedure for measurement of P31 and P32 in plant material. *Analyt. Chem.* 20: 559-60.
 - (4) MacKENZIE, A. J., AND DEAN, L. A. 1950 Measurement of P32 in plant material by the use of briquettes. *Analyt. Chem.* 22: 489-90.
 - (5) MACY, P. 1936 Quantitative mineral requirements of plants. *Plant Physiol.* 11: 749-764.
 - (6) MIDGLEY, A. R. 1931 Movement and fixation of phosphates in relation to permanent pasture fertilization. *Jour. Amer. Soc. Agron.* 23: 788.
 - (7) NELLER, J. R. 1947 Mobility of phosphates in sandy soils. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 227-230.
 - (8) RUSSELL, E. J. 1950 Soil Conditions and Plant Growth. London.
 - (9) SPINKS, J. W. T., AND BARBER, S. A. 1948 Study of fertilizer uptake using radioactive phosphorus. *Sci. Agr.* 28: 79-87.
 - (10) STEPHENSON, R. E., AND CHAPMAN, H. D. 1931 Phosphate penetration in field soils. *Jour. Amer. Soc. Agron.* 23: 759-770.
 - (11) STRZEMIENSKI, K. 1948. Soil phosphate uptake as influenced by phosphatic fertilizer. *Nature* 162: 932.
 - (12) WAYNICK, D. D., AND LEAVITT, H. F. 1930 Penetration of phosphorus in representative soil types. *Calif. Citrogr.* 15: 152-154.

ELONGATION OF SEEDLINGS AS A BIOLOGICAL TEST OF ALKALI SOILS: I. EFFECTS OF IONS ON ELONGATION

MOHAMED NAGUIB HASSAN AND ROY OVERSTREET

University of California¹

Received for publication July 31, 1951

The presence of alkali, or undesirably high concentrations of salts, is very common in soils of the arid and semiarid regions of the world. The vegetation of these soils may be severely restricted by the presence, currently or in the past, of soluble salts of calcium, magnesium, potassium, and sodium. The salts of sodium occur by far the most abundantly; hence, the term "alkali soils."²

In general, alkali soils are potentially very fertile, and because of the huge acreages involved, they constitute an important and relatively unexploited natural resource. For this reason, those aspects of alkali soils affecting the growth of crops have been the subject of study by soil scientists and plant physiologists for many years.

The property of many alkali soils which obviously may restrict the growth of plants is the excessive concentrations of soluble salts and the resulting high osmotic pressure of the soil solution. This condition was recognized very early by Hilgard, who studied the origin and mode of accumulation of soluble salts in soils and the tolerance of plants to soluble salts occurring in alkali soils. He found that the soluble salts were mixtures of NaCl, Na₂SO₄, and NaHCO₃. The ratios of the different salts varied widely from place to place. Hilgard (8) assumed from field observations and chemical analyses of soils that the effects on plants produced by different salts also varied greatly; that is, "white alkali" (NaCl, Na₂SO₄, MgCl₂) is much milder in its effect on plants than is "black alkali" (caused by the presence of Na₂CO₃).

Following Hilgard, other investigators studied the effects of solutions of high osmotic pressures on the germination of seeds and the growth of plants. Work of particular interest to the subject of this paper is reviewed in Rudolfs' report (17) in 1925 dealing with the influence of salts on the growth of plants.

In recent years, Magistad, Wadleigh, and others (3, 4, 7, 14, 15, 21, 22, 23) have made contributions to the subject. In essence, these investigators concluded that retardation of the growth of plants in saline soils is due primarily to osmotic effects, although important differences between salts such as NaCl, NaHCO₃, CaCl₂, and MgCl₂ are recognized.

A property of alkali soils not emphasized by the earlier investigators but which

¹ This paper is based on work performed under Contract No. AT(11-1)-34, Project No. 5, with the Atomic Energy Commission. The work was taken from a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of doctor of philosophy in soil science, 1951.

² The terminology used in this paper is that employed by Kelley (13). The term "alkali soil" denotes soil which contains an excess of soluble salts or abnormal percentages of exchangeable Na⁺, or both.

assumed increasing importance as principles of ion-exchange were better understood is the status of soil-adsorbed sodium. Hissink (9), Gedroiz (5), d'Sigmond (18), and Kelley (12, 13) pointed out the role of the exchangeable ions as an aspect of alkali soils. The highly toxic effect of adsorbed sodium on the growth of barley, cow peas, and alfalfa was demonstrated by Kelley and Thomas (11). These workers also showed by means of greenhouse experiments that a nonsaline soil high in exchangeable sodium was extremely toxic to barley seedlings. These investigations were followed and confirmed by the researches of Gedroiz (6), Ratner (16), Joffe and Zimmerman (10), Thorne (19), Bower and Wadleigh (2, 25). In short, it has been concluded that exchangeable sodium in amounts varying from 10 to 70 per cent of the exchangeable cations may inhibit the growth of a variety of plants. On the other hand, considerable uncertainty exists as to the reason for the toxic effect of adsorbed sodium. The following may be considered: (a) the adsorbed sodium is absorbed by the plant and in some way interferes with the plant's metabolism, (b) the absorption of essential elements such as potassium and calcium may be reduced by the presence of high concentrations of adsorbed sodium, (c) soils high in adsorbed sodium may actually deprive seedlings of necessary elements such as potassium and calcium initially contained in the seed.

The failure of crops in a given alkali soil may be due to a variety of factors. Moreover, the relative importance of the contributing factors may be very difficult to assess. For example, the deleterious effects of osmotic pressure *per se* or of individual elements are unknown. Also, the relative importance of the amount of exchangeable sodium, or the inaccessibility of essential elements induced by the presence of sodium, is far from being quantitatively related to growth inhibition observed in random situations.

In view of the extreme importance of these questions in connection with the reclamation of alkali lands, the research reported in this paper was devoted to the evaluation of some of these contributing factors as single entities.

The problem was approached by studying the elongation of seedlings over short periods during which the germinating seedlings were adequately supplied with nutrients from the seed reserve to make consistently satisfactory growth.

Thus, external factors in the environment of the seedling may be varied at will. The seed may be considered as a reservoir of all required nutrients which has comparable properties among all experimental variations. Even so, it has been found that changes in the external environment, such as the kind and quantity of soluble salts in sand cultures, result in measurable differences in rates of elongation of the roots and hypocotyls of the seedlings. This technique permits conclusions concerning the contribution of single components of the seedling's environment to its ability to grow.

EXPERIMENTAL TECHNIQUE

As has been indicated, the technique of the present investigation required the selection of a plant and a time during which the germinating seedling would have an adequate supply of seed-borne nutrients, as judged by the following

criteria: at some time interval during the early stages of germination, the rate of growth should be the same whether the culture medium consisted of sand moistened with distilled water, of sand moistened with a complete nutrient solution, or of a recognized fertile soil moistened to its moisture equivalent. The general plan for determining factors contributing to growth inhibition was to place such a plant, for the selected time, in sand cultures moistened with a variety of solutions. It was thought that any reduction in the growth rate below that observed with distilled water (complete culture or fertile soil) could be attributed to specific deleterious effects of the salts or ions of the media.

With this object in view, the germination and growth habits of a large variety of seeds were studied.

Of the plants investigated, lima bean (*Phaseolus limensis*) and radish (*Raphanus sativus*) showed the greatest promise. The radish plant was finally chosen because of the inconveniently large size and poorer germination of the bean

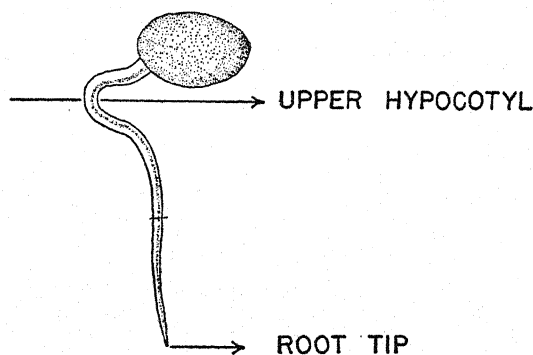


FIG. 1. RADISH SEEDLING AFTER 36 HOURS' GERMINATION

seeds. The different steps necessary for standardization of the experimental technique follow.

Measures or indexes of growth

For the radish seedlings under consideration, the following indexes of growth might be used: 1. Increase in fresh weight of the seedling; 2. Decrease in dry weight of the seedling; 3. Increase in length of the radicle; 4. Increase in volume of the radicle.

Experimentation showed that the increase in length of the radicle could be measured most conveniently, and this index, therefore, was adopted.

The measurement of radicle lengths required careful standardization. That is, such measurements must concern the distance between two very definite points on the radicle. One of these points is obviously the root tip. The selection of the second point may vary from one plant species to another. For example, in lima bean, the junction of the hypocotyl and the cotyledons was found to be most appropriate. In the radish seedling, the reference point selected was that where the hypocotyl curves itself approximately 180°, as shown in figure 1.

Ordinarily, the growth of the radicle in radish seedlings is not straight. For this reason, it was found convenient to use a thread which could be run exactly on the radicle throughout its length and then subsequently stretched on a Dietzgen scale calibrated into intervals of 0.4 mm.

Method of germination

All steps of the experimental procedure were carried out in a germination chamber maintained at 26–27°C. The radish seeds were germinated on moist

TABLE 1
Effect of length of growth period on elongation of radish seedlings

	WASHED NEVADA WHITE SAND + H ₂ O		WASHED NEVADA WHITE SAND + HOAGLAND		HANFORD FINE SANDY LOAM	
Growth period.....hr.	24	36	24	36	24	36
Elongation.....mm.	53.4	69.6	52.9	71.5	53.6	109.1

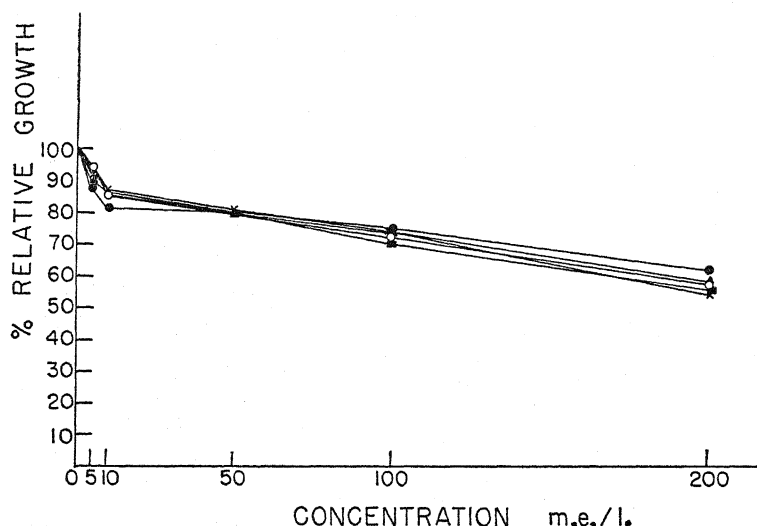


FIG. 2. EFFECT OF INCREASING CONCENTRATION OF NaCl ON THE RELATIVE ELONGATION OF RADISH SEEDLINGS. Five replicates

filter paper. The paper, which was circular and of 60-cm. diameter, was cut into half circles. One of the halves was placed over a screen supported by a glass rack standing in a rectangular pyrex pan containing distilled water. The ends of the filter paper were dipped into the water. The seeds were uniformly spread on the paper and were then covered with the other half of the filter paper so that its ends also dipped into the water. The pan containing the seeds was then covered by another rectangular pyrex pan and allowed to stand in the germination chamber for exactly 36 hours. At the end of this period the average length of the seedlings was approximately 11–12 mm. At this stage the seedlings were taken for experimentation.

The moistened sand cultures were contained in large pyrex crystallizing dishes (150 by 75 mm.). The sand was placed to a depth of approximately 1 inch in each dish, and 50 seedlings were evenly distributed on the surface then covered with the sand to a depth of 1 inch. The crystallizing dishes were covered with glass moisture dishes (200 by 70 mm.) and placed in the germination chamber for exactly 24 hours. The seedlings were then removed carefully, and the lengths of radicles were measured. The increase in the length of the radicle during the 24-hour period was calculated as the difference between the mean of the initial length and the mean of the final length of the seedling.

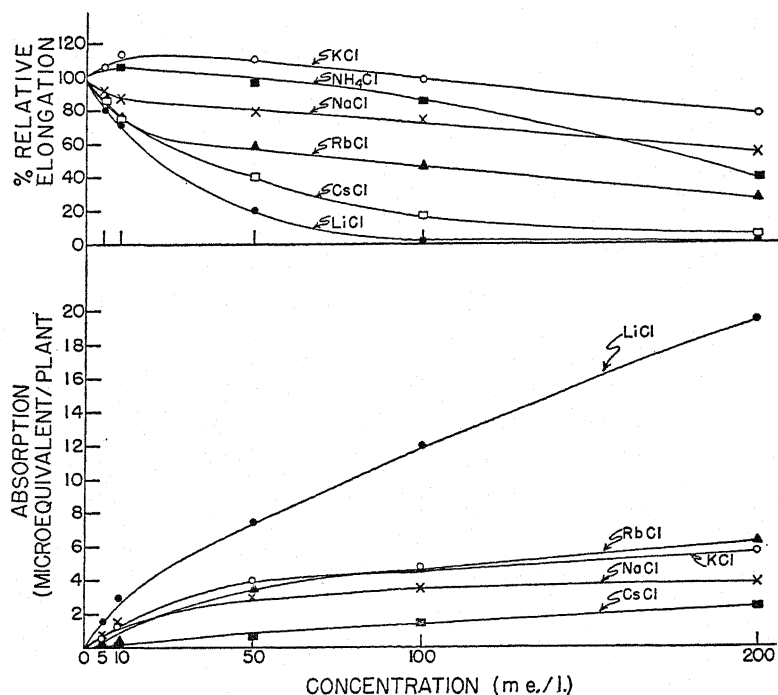


FIG. 3. EFFECT OF INCREASING CONCENTRATION OF CHLORIDE SALTS OF ALKALI ELEMENTS ON THE RELATIVE ELONGATION AND ABSORPTION BY RADISH SEEDLINGS

Choice of water content of sand cultures

Whenever soil was used as the culture medium, the soil was arbitrarily moistened to the moisture equivalent. In all sand cultures, the sand was moistened to a P_w of 10 per cent. The selection of this moisture content was based on the following data: mean elongation of radish seedlings at 26°C. in sand cultures moistened with distilled water to a P_w of 4 per cent, 43.1 mm.; 6 per cent, 49.5 mm.; 8 per cent, 47.7 mm.; 10 per cent, 53.4 mm.; 12 per cent, 47.8 mm.

Selection of age of seedlings for experimental treatments

The selection of the 24-hour growth period was based on the data in table 1, which shows the elongation at 26°C. of radish seedlings in sand moistened with

distilled water, in sand moistened with Hoagland solution, and in Hanford fine sandy loam moistened to its moisture equivalent.

From table 1 it is apparent that at some time between 24 hours and 36 hours the elongation of the radish seedling becomes a function of the nutrient status in the external medium. Up to a period of 24 hours, only slight growth of the hypocotyl was observed. In the neighborhood of 30 hours, elongation of the hypocotyl became very marked, and at the end of 36 hours elongation of the hypocotyl greatly predominated over that of the radicle.

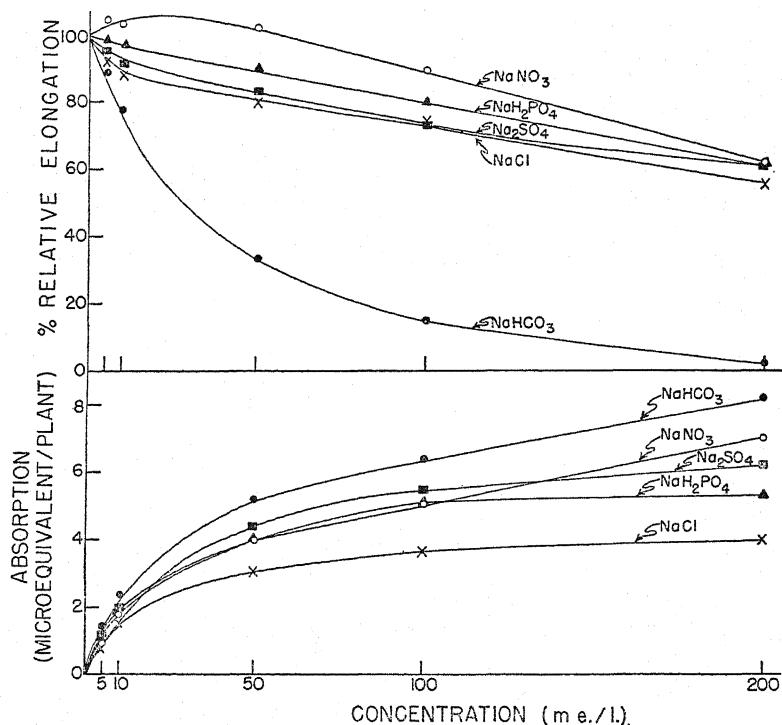


FIG. 4. EFFECT OF INCREASING CONCENTRATION OF CHLORIDE SALTS OF ALKALINE EARTH ELEMENTS ON THE RELATIVE ELONGATION AND ABSORPTION BY RADISH SEEDLINGS

Statistical significance of measurements of elongation

Radish seedlings in sand cultures moistened with different concentrations of NaCl showed the following relative elongation, based on 100 per cent for distilled water: 0.005 *N* NaCl, 94.3 per cent; 0.01 *N*, 84.6 per cent; 0.05 *N*, 79.7 per cent; 0.1 *N*, 72.1 per cent; 0.2 *N*, 56.9 per cent.

The maximum standard error obtained for these data was 1.3 mm. with a coefficient of variation 2.4 per cent. The probability (*P*) was found to be 0.05. This means, for example, that the difference between the distilled water treatment and the 0.005 *N* treatment was significant at the 5 per cent level.

In figure 2 are plotted curves showing the relative elongation of radish seedlings as a function of the concentration of NaCl in sand cultures for five experiments run at different times to ascertain the reproducibility of the method.

EXPERIMENTS

A series of experiments were carried out to determine the effects of chlorides of the alkali metals on elongation of the seedlings in sand cultures. Elongation studies were also made with chloride salts of the alkaline earth elements except

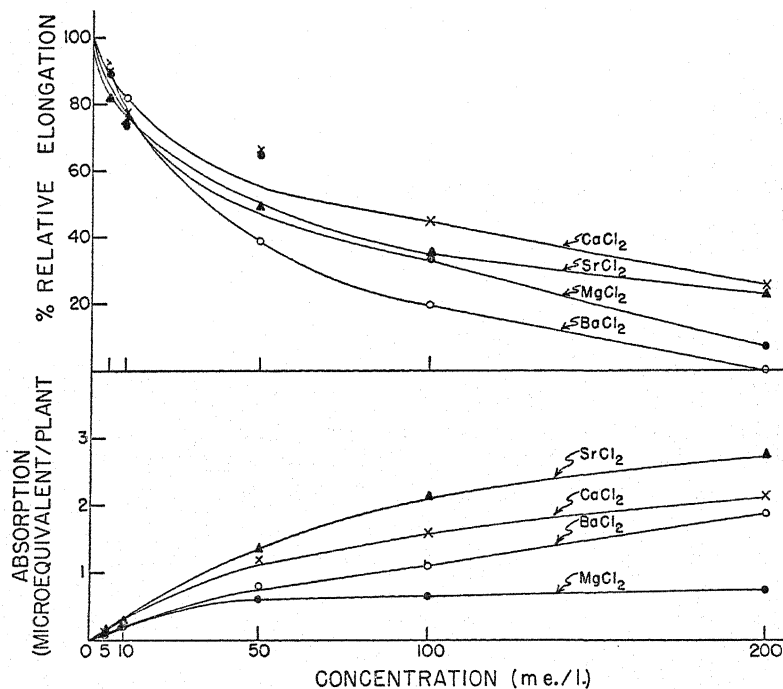


FIG. 5. EFFECT OF INCREASING CONCENTRATION OF DIFFERENT SODIUM SALTS ON THE RELATIVE ELONGATION AND ABSORPTION BY RADISH SEEDLINGS

beryllium. Sand moistened with distilled water and sand moistened with different concentrations of each salt up to 0.2 *N* were used. For all salt solutions, the relative elongation was calculated as the percentage of the growth in distilled water. The results are presented in figures 3 and 4.

After the elongation measurements were made, the seedlings were ashed and analyzed for the specific cation in question. The resulting absorption curves are shown in figures 3 and 4.

To bring out the effects of the anion in a single salt solution on the elongation of the radicle, the following salts of sodium and calcium were also studied by means of sand culture technique: NaNO_3 , NaCl , NaHCO_3 , NaH_2PO_4 , Na_2SO_4 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{OH})_2$, and CaSO_4 . The curves for the elongation in pres-

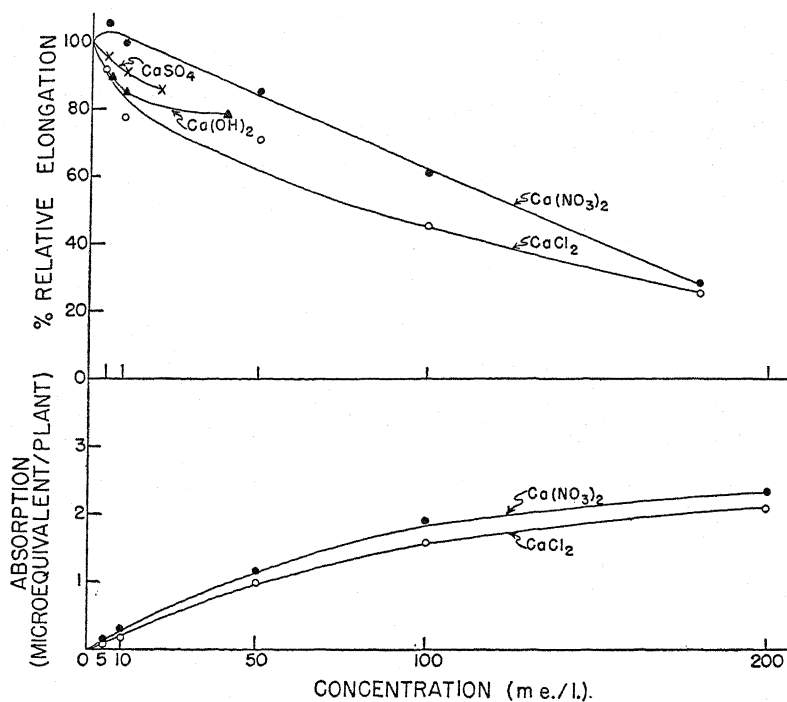


FIG. 6. EFFECT OF INCREASING CONCENTRATION OF DIFFERENT CALCIUM SALTS ON THE RELATIVE ELONGATION AND ABSORPTION BY RADISH SEEDLINGS

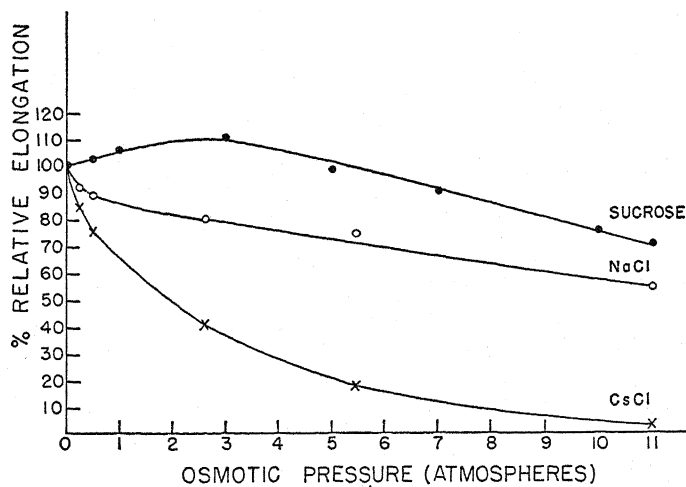


FIG. 7. EFFECT OF INCREASING OSMOTIC PRESSURE OF SUCROSE, NaCl, AND CsCl ON THE RELATIVE ELONGATION OF RADISH SEEDLINGS

ence of the sodium salts are presented in figure 5 and those of calcium salts in figure 6. The corresponding absorption curves are shown in the same figures.

As a possible aid in interpreting the influence of single salt solutions on radicle

elongation, the relative elongation in sand cultures moistened with sucrose solutions at different osmotic pressures was determined. These results are presented in figure 7, together with the data for NaCl and CsCl in comparable units.

DISCUSSION AND CONCLUSIONS

Figure 3 shows a very wide divergence in the effects on elongation of single chloride salts of the alkali metals. Over a considerable range of concentration, KCl stimulates elongation more than does distilled water. To a lesser extent, the same is true for NH_4Cl . At higher concentrations, however, these salts effect a lowering of the relative elongation. The single chloride salts of the other members of the alkali group diminish elongation throughout the entire concentration range, the relative effects being in the order $\text{LiCl} > \text{CsCl} > \text{RbCl} > \text{NaCl}$. According to a recent report from the Riverside Citrus Experiment Station (1), it was found that Li in concentrations of 0.05–0.1 ppm. is toxic to citrus trees.

The observed stimulation of seedling elongation by dilute solutions of KCl is in harmony with the observations of Rudolfs (17) for soybeans and watermelon seedlings. It conforms also to the recently projected theory that potassium enhances cell division (24). It is of further interest to compare the behavior of the chloride salts of Li, Na, K, Rb, and Cs observed in this research with the effects of the same salts on cell elongation in *Avena* coleoptiles reported by Wuhrman (26). Wuhrman observed a maximum relative elongation of the cells with KCl and a rapid diminution in elongation from K to Li and from K to Cs. Wuhrman concluded that growth in presence of Rb and Cs is less than that in presence of K, because these ions are less hydrated. He concluded also that growth in presence of Na and Li is less than that with K because of the rapid absorption and the specific toxic effects of these two elements on the formation of heteroauxin in the coleoptile. A comparison of the growth curves of figure 3 indicates that the effects of the alkali metals on the elongation of radish seedlings are consistent with the observations of Wuhrman. In a special experiment conducted in this laboratory a series of elongation determinations were carried out in the presence of LiCl and indolacetic acid. The concentration of LiCl was varied from 0.005 *N* to 0.05 *N* and the indolacetic concentration from 10^{-14} *M* to 10^{-6} *M*. In all cases the elongation in presence of indolacetic acid was less than that in LiCl alone. This experiment would seem to cast some doubt on the idea that Li inhibits the production of heteroauxin, at least in radish seedlings.

It was noted in the elongation experiments with RbCl and CsCl that a dense red pigment developed in the cotyledons of the seedlings. This was also true, but to a much less extent, with LiCl.

An anatomical study, to be reported elsewhere, revealed that lithium-treated roots showed evidence of early maturation. This was evident from the appearance of lignified xylem tissues and the vacuolization of the cortical cells in the lithium-treated roots. It was noted also that the procambial cells of the lithium-treated roots were ruptured. It was impossible, from examination of the longitudinal and cross sections, to conclude whether or not there was an effect on cell division. There was, however, a definite effect on cell elongation of the lith-

ium-treated roots, although the cells, especially the cortical, had a larger diameter. It cannot, of course, be presumed that the anatomical effects of NaCl, RbCl, and CsCl are the same as those observed with LiCl. It is entirely possible that the effects are different for all members of the alkali group.

The absorption curves of figure 3 suggest that for a given element there is a negative correlation between the seedling elongation and the absorption of the element. With the chlorides of Li, Na, Rb, and Cs, the rate of elongation is reduced, the greater the amount of the element absorbed. On the other hand, there seems to be no correlation between the rate at which an element is absorbed and its effect on elongation. In this connection, it should be noted that the reduction of elongation was in the following order: $\text{LiCl} > \text{CsCl} > \text{RbCl} > \text{NaCl} > \text{KCl}$, whereas the order for absorption rates was $\text{LiCl} > \text{KCl} > \text{RbCl} > \text{NaCl} > \text{CsCl}$.

Elongation of the radish seedlings in presence of RbCl is different from that in presence of CsCl, which in turn is different from the elongation in KCl. Nevertheless, the absorption of Rb^+ is almost the same as that of K^+ , but the absorption of Cs^+ is considerably less than that of Rb^+ or K^+ . This observation alone would throw doubt on the possibility that potassium, rubidium, and cesium behave very similarly in plant functions.

The curves of figure 4 indicate somewhat less variability in effects on elongation among the chloride salts of the alkaline earth elements than among the members of the alkali group. In the lower concentration range, the depression in elongation follows the order $\text{BaCl}_2 > \text{SrCl}_2 > \text{MgCl}_2 > \text{CaCl}_2$; in the higher concentration range, it follows the order $\text{BaCl}_2 > \text{MgCl}_2 > \text{SrCl}_2 > \text{CaCl}_2$. Furthermore, although the alkali metal series was found to have the same sequential inhibitory influence as that observed by Wuhrman for the *Avena* coleoptile, the sequence for the alkaline earths was different. Wuhrman observed maximum relative elongation of *Avena* cells in the presence of MgCl_2 , but our roots showed maximum elongation in the presence of CaCl_2 .

Of possible significance is the fact that in the present experiments the relative elongation of each group of elements (alkali and alkaline earth group) shows a definite pattern, if plotted as a function of the atomic number, the ionic radius, or the lyotropic number of each element or ion. The maximum relative elongation is with the elements potassium and calcium. The absorption of these cations by radish seedlings, however, does not follow a consistent pattern. Slight development of red pigment in the cotyledons was observed with MgCl_2 .

The absorption curves of figure 4 reveal, as with the chlorides of the alkali salts, that for a single element the greater the amount absorbed, the greater is the depression of elongation. Similarly with this group there is no correlation between the rate at which an element is absorbed and its effect on relative elongation.

The curves of figure 5 show that the different sodium salts depress elongation of the radish seedlings in the order $\text{NaHCO}_3 > \text{NaCl} > \text{Na}_2\text{SO}_4 > \text{NaH}_2\text{PO}_4 > \text{NaNO}_3$. Stimulation was observed in the lower concentration range of NaNO_3 . The extremely toxic effect of NaHCO_3 is in agreement with the observations of

Magistad *et al.* (14, 15) on a variety of plants grown on sand cultures over long periods. When the growth curves are compared with the absorption curves of figure 5 it becomes evident that among the different salts there is no relation between depression of growth and the amount of Na^+ absorbed. Development of dense red pigment was observed with Na_2SO_4 . With the higher concentrations of NaHCO_3 , the root tips were stunted and gave off a putrid odor.

The curves of figure 6 indicate a maximum depression of growth in presence of CaCl_2 and a minimum depression in presence of $\text{Ca}(\text{NO}_3)_2$. Moreover, when these curves are compared with the absorption curves in the same figure, no correlation between the rate of calcium absorption and the growth of the radish seedlings is evident.

From figure 7, comparing the relative elongation of seedlings in sucrose solutions and in NaCl and CsCl solutions at osmotic pressures varying from 1 to 11 atmospheres, it seems evident that the popular theory attributing the effects of salt solutions to a restriction in availability of water is untenable for the type of elongation under study [see Uhvits (20) and Wadleigh *et al.* (21, 23)]. It appears that the elongation dealt with in this research is relatively insensitive to the osmotic pressure of the sucrose solution up to values of about 11 atmospheres. On the other hand, elongation may be greatly reduced at rather low concentrations of certain salts, namely, LiCl and CsCl . The stimulation observed in the elongation of radish seedlings at sucrose concentrations from 1 to 4 atmospheres may have been due to absorption of sucrose and resulting increased activities of the cells.

To summarize, the experiments with single salts lead to the conclusions that the depressing effect of salt on the elongation of the radish seedlings studied is not due primarily to increased osmotic pressure of the culture medium with a resulting restriction in availability of water to the plant. It appears more reasonable that the different elements comprising the salts exert an inhibiting effect in some way upon one or more steps of the metabolic processes in the plant. In general, there is a much greater divergence in the inhibition effect with cations than with anions, except in the case of HCO_3^- .

The present technique has been extended to an examination of the effects of adsorbed ions and mixtures of salts on elongation. In addition, correlations have been sought between elongation of the seedlings in alkali soils and crop yields. The same technique has been employed to study the effect of radioactive elements. This work will be reported in later publications.

REFERENCES

- (1) ALDRICH, W. W., ET AL. 1951 Lithium toxicity in citrus. *Soil Sci.* 71: 291-295.
- (2) BOWER, C. A., AND WADLEIGH, C. H. 1949 Growth and cationic accumulations by four species of plants as influenced by various levels of exchangeable sodium. *Soil Sci. Soc. Amer. Proc.* (1948) 13: 218-227.
- (3) GAUCH, H. G., AND WADLEIGH, C. H. 1944 Influence of high salt concentrations on growth of bean plants. *Bot. Gaz.* 105: 379-387.
- (4) GAUCH, H. G., AND WADLEIGH, C. H. 1945 Effect of high concentrations of Na^+ , Ca^{++} , Cl^- , SO_4^{--} on ionic absorption by bean plants. *Soil Sci.* 59: 139-153.
- (5) GEDROIZ, K. K. 1918-1919 Contribution to our knowledge of the absorptive capacity

- of the soil: I. *Zhur. Opytn. Agron.* [Russian] 19: 269-322; 20: 31-58. [Translated from Russian by S. A. Waksman, mimeographed and distributed by U. S. Department of Agriculture.]
- (6) GEDROIZ, K. K. 1931 Lehre von Adsorptionvermögen der Boden. *Kolloidchem. Beihefte* 1931: 317-448. (Translated from Russian by H. Kuron.)
 - (7) HAYWARD, H. E., AND WADLEIGH, C. H. 1950 Plant growth on saline and alkali soils. *Advances in Agron.*
 - (8) HILGARD, E. W. 1912 Soils. The Macmillan Company, London.
 - (9) HISSINK, D. J. 1922 Beitrag zur Kenntnis der Adsorption-vorgänge in Boden. *Internatl. Mitt. Bodenk.* 12: 81-172.
 - (10) JOFFE, J. S., AND ZIMMERMAN, J. 1945 Sodium, calcium and magnesium ratios in the exchange complex. *Soil Sci. Soc. Amer. Proc.* (1944) 9: 51-55.
 - (11) KELLEY, W. P., AND THOMAS, E. E. 1928 Reclamation of the Fresno type of black alkali soils. Calif. Agr. Exp. Sta. Bul. 455.
 - (12) KELLEY, W. P. 1948 Cation Exchange in Soils. Reinhold Publishing Corporation, New York.
 - (13) KELLEY, W. P. 1951 Alkali Soils, Their Formation, Properties and Reclamation. Reinhold Publishing Corporation, New York.
 - (14) MAGISTAD, O. C., AND REITEMEIER, R. F. 1943 Soil solution concentrations at the wilting point and their correlation with plant growth. *Soil Sci.* 55: 351-360.
 - (15) MAGISTAD, O. C. 1945 Plant growth relations on saline and alkali soils. *Bot. Rev.* 11: 161-230.
 - (16) RATNER, E. I. 1935 Influence of exchangeable sodium in the soil on its properties as a medium for plant growth. *Soil Sci.* 40: 459-471.
 - (17) RUDOLFS, W. 1925 Influence of water and salt solutions upon absorption and germination of seeds. *Soil Sci.* 20: 15-37.
 - (18) D'SIDMOND, A. A. 1938 The Principles of Soil Science. Thomas Murby Co., London.
 - (19) THORNE, D. W. 1945 Growth, nutrition of tomato plants as influenced by exchangeable sodium, calcium and potassium. *Soil Sci. Soc. Amer. Proc.* (1944) 9: 185-189.
 - (20) UHVITS, R. 1946 Effects of osmotic pressure on water absorption and germination of alfalfa seeds. *Amer. Jour. Bot.* 33: 278-285.
 - (21) WADLEIGH, C. H., AND AYERS, A. D. 1945 Growth and biochemical composition of bean plants as conditioned by soil moisture tension and salt concentration. *Plant Physiol.* 20: 106-132.
 - (22) WADLEIGH, C. H., GAUCH, H. G., AND MAGISTAD, O. C. 1946 Growth and rubber accumulation in guayule as conditioned by soil salinity and irrigation regime. U. S. Dept. Agr. Tech. Bul. 925.
 - (23) WADLEIGH, C. H., GAUCH, H. G., AND STRONG, D. G. 1947 Root penetration and moisture extraction in saline soils by crop plants. *Soil Sci.* 63: 341-349.
 - (24) WADLEIGH, C. H. 1949 Mineral nutrition of plants. *Ann. Rev. Biochem.* 1949: 655-678.
 - (25) WADLEIGH, C. H., AND BOWER, C. A. 1950 Influence of calcium ion activity in water cultures on the intake of cations by bean plants. *Plant Physiol.* 25: 1-12.
 - (26) WUHRMAN, K. 1937 Action of Cations on Cell Elongation. Diss. E. T. H., Zurich.

BOOKS

The American Economy. By A. F. YOUNGSON BROWN. Library Publishers, New York, 1952. Pp. 208. Price \$4.75.

This book is an outcome of one of 20 Commonwealth Fund fellowships awarded annually for British students to study in American universities. The author, quite objectively, has covered the period from the Civil War to 1940. The presentation is concise and attractive. The most interesting phases of the discussion from the soil-plant scientist's standpoint are those dealing with the peopling of America; agriculture, its progress, decline, and stabilization; depression and the New Deal; and the American way of life. The appendix shows graphs of population, income per head, steel production, and export trade, and a list of authors quoted in the text. The book is highly interesting reading.

Bibliography of Differential Thermal Analysis. Research Series No. 21. By W. J. SMOTHERS, YAO CHIANG, AND ALLAN WILSON. Institute of Science and Technology, University of Arkansas, Fayetteville, 1951. Pp. 44.

To information on the development of this method of analysis, equipment employed, variables, and use of method, is attached a bibliography of 165 references. In addition, the bulletin contains indexes of prepared mineral mixtures, chemically treated minerals, chemical mixtures, fuel and carbonization products, metals, minerals, and rocks.

Essays in Provocation. By GLENN E. HOOVER. Philosophical Library, New York, 1951. Pp. 226. Price \$3.

This volume contains copies of 57 letters and five essays and addresses by the author. The letters are addressed to various and sundry persons connected with government, industry, publications, and other agencies, including Raymond Moley, General Electric, J. P. Morgan and Co., Harry S. Truman, Business Week, Fortune, Sun Oil Co., Senators Paul Douglas and Margaret Smith, Secretary of State Acheson, and Norman Thomas. In each letter the author picks out some fallacy in a public statement of the person to whom the letter is addressed. By so doing he performs the double purpose of enlightening the person involved and now, in this book, the public at large. The subjects dealt with include: Are depressions beyond governmental control, should paper money be redeemable in gold, do banks create money, quotas as a remedy for farm surpluses, future of U. S. tariffs, how to make food scarce, sugar and statism, potatoes and the Brannan plan, and salaries of public employees. The essays have to do with German economy, Henry George, and Jeffersonian democracy. The net result is a very stimulating presentation of many problems that face the nation.

✓ *Handbook of Ohio Experiments in Agronomy.* Ohio Agricultural Experiment Station, Wooster, Ohio, 1951. Pp. 204. Price, paper bound, \$1.

Virtually all the members of the agronomy department contributed to the

preparation of this very comprehensive report on research accomplishments of the department. The contents are divided into eight sections dealing with lime, fertilizers and manures, corn and soybeans, small grains, meadows and pastures, crop residues and green manuring, crop rotation, and soil and water conservation. Data are shown in 219 tables, each of which deals with a separate topic. A former summary of the same type enjoyed wide popularity, and this issue is certain to be equally well received. The Ohio Agriculture Experiment Station may well be proud of this publication and the research accomplishments reported in it.

Man and the Living World. Second Edition. By E. E. STANFORD. The Macmillan Company, 1951. Pp. 863, figs. 483. Price \$5.50.

This book is designed for an elementary course in biology. It covers a very wide range of subjects from the origin of life to a detailed survey of the biological resources of the United States. The book is divided into the following units: science and living things, the plant as a manufacturer of foodstuffs and raw materials for industry, the human body, maintenance of health, microorganisms, the animal and plant kingdoms, evolution and heredity, and domestication and breeding of plants and animals. Its 35 chapters cover such widely different subjects as reproductive systems, foods and poisons, bacteria and disease, worms, lower forms of plant life, evolution and heredity, and soil, forest, and wildlife resources. It is difficult to conceive of any one man being able to present such a complete picture of the field of biology. Certainly, if a beginning college student is able to grasp the contents of this volume, he will be well on his way toward an understanding of his relationship to his environment.

North of the Circle. By FRANK ILLINGWORTH. Philosophical Library, New York, 1952. Pp. 254, plates 32. Price \$4.75.

The author of this book points out that "once a man has wintered in the arctic he'll always return. Living up there becomes a state of mind." One of the reasons for this is found in the release from dense populations where four persons may be considered a crowd. The several chapters define conditions as they apply to prospectors, women, doctors, hunters, farmers, Eskimos, Lapps, and other groups of people. The farming phase is of special interest to soil-plant scientists. "Beyond the polar circle there is continuous daylight during the short summer when the heat may reach 100° F. in the shade and two or three crops of hay can be brought to maturity, where the farmer of southern latitudes can raise only one or two." During the winter, milk is put out in pans to freeze for storage and transport. But "the milk supply drops steeply when the sun disappears." Surprisingly large yields of the standard crops are produced. The strategic importance of the North in terms of military needs is stressed, as are also the potentialities in mineral production. The arctic regions appear to be growing warmer and, in proportion as this occurs, still more importance attaches to them. This is a highly interesting book which virtually everyone would enjoy.

Official Publication, Association of American Control Officials, No. 5. B. D. Cloaninger, Sec.-Treas., Clemson, S. C., 1951. Pp. 79. Price, paper-bound, \$1.

This is the proceedings of the annual convention held at Washington, D. C., October 6, 1951. Among the subjects considered were a uniform fertilizer bill, minor elements, fertilizer through irrigation, acid-insoluble ash and carbonates in mixed fertilizers, and reports of investigators and committees. The acid-insoluble ash in fertilizers, as reported by K. G. Clark and his associates, was found to range between 11 and 787 pounds a ton.

✓ *Phosphates in Agriculture*. Revised Edition. By VINCENT SAUCHELLI. The Davison Chemical Corporation, Baltimore, 1951. Pp. 176, figs. 43. Price \$2.50.

The primary purpose of this manual is to serve the needs of the personnel of the Davison Chemical Corporation. But a great many other persons who have to do with the manufacture, sale, and use of fertilizers will find it of much interest and value. Over the years the author of this book has had abundant opportunity to study the subject in all its aspects and his wide knowledge of phosphorus and its uses is clearly shown in this revised edition. The illustrations and tables are of special interest, and some highly important references are given. All students of fertilizers will want a copy close at hand.

Proceedings, First National Institute of Animal Agriculture. Purdue University' Lafayette, Indiana, 1951. Pp. 108. Paper bound.

This is a complete report of papers presented before the Institute held at Purdue University, April 16-18, 1951. These papers dealt with aims and objectives, diet, animal agriculture economics, higher production, animal agriculture and the soil, food and farm policy in relation to national economy, feed utilization by livestock and poultry, significance of animal products to human nutrition, problems in human nutrition, and the job to be done. Material of interest to a great variety of persons will be found in this booklet.

Range Management, Principles, and Practices. By A. W. SAMPSON. John Wiley and Sons, Inc., New York, 1952. Pp. 570, figs. 111. Price \$7.50.

As the author points out, "This book has been a long time in the making." Only a man with wide experience in field research could write as good a book as this on range management. The book deals with the subject in broad terms. The four parts are headed: range management in perspective, native range forage plants, improvement and management of range and stock, and protection of land resources and range livestock. Each of the 24 chapters is well illustrated and has a long list of appended references. The more important grasses and other forage plants, including the poisonous ones, are described in considerable detail. The problems of reseeding and of systematic range management are carefully considered. Among the very interesting sidelights is a table showing data on original and recent populations of big game, including the bison, the number of which, in 1700, was estimated at 60 million, in comparison with 4,900 in 1941. This is an interesting and valuable book, and it is certain to enjoy a wide reading.

Reconnaissance Soil Survey of Japan, Northern Honshu Area. Report No. 110-G. By HARRY C. MORTLOCK. General Headquarters Supreme Commander for the

Allied Powers, Natural Resources Section, Tokyo, 1951. Pp. 71, figs. 9, plates 2, 8 soil maps in color.

This is one of a series of soil surveys presumably designed to cover the entire land area of Japan. This survey covers 21.5 per cent of the area. Sixty-three soil associations are recognized. The gray to black alluvial soils are of most agricultural importance. The high terraces are occupied by gray-brown podzolic soils. Planosolic soils occupy the paddy-rice fields. More than 70 per cent of the land area is covered with lithosols. The principal crop is rice, but barley, soybeans, potatoes, buckwheat, and tobacco are also grown. The area averages 1 head of draft cattle for each 4.8 hectares and 1 horse for each 3.6 hectares of cropland. Chickens and rabbits average 2.3 a farm. Seventy per cent of the land is in forest, of which 18 per cent is coniferous.

Subtropical Gardening in Florida. By NIXON SMILEY. University of Miami Press, Miami, Florida, 1951. Pp. 182, plates 20. Price \$4.

This is a beautifully illustrated and well-stated presentation of the changes that are necessary in the thinking and practice of the northerner who goes to southern Florida to live. As the author points out, one should forget the tulip, rhododendron, and lilac, and cultivate an interest in the canna, hibiscus, and bougainvillea. Bluegrass, bentgrass, and fescue yield to St. Augustine, centipede, and Bermuda grasses. Palms, orchids, and a great variety of climbing plants and flowering trees are at the nature-lover's disposal. But some of the most interesting adventures are associated with the growing of the lychee, orange, avocado, mango, and papaya. One must be prepared for mosquitoes, sandflies, chinchbugs, brown patch, and a considerable variety of other insect and fungus pests. But the persistent gardener is rewarded by such a variety of beautiful flowers and delicious fruits that he feels well paid for his efforts, according to the author. Anyone who contemplates going to Florida will certainly want a copy of this very attractive book, and others too will enjoy reading it.

The Tohoku Journal of Agricultural Research. Volume 1, No. 2. Faculty of Agriculture, Tohoku University, Sendai, Japan. December, 1950. Pp. 151-232.

All articles in this journal are printed in English. Papers on agronomy, animal husbandry, fisheries, and agricultural chemistry are included. Among those of interest to soil-plant scientists are "Study on sexual affinity among rice varieties" and "Effects of heating and dehydration on the constitution and availability of scarcely soluble phosphates, III and IV." The Journal is issued twice yearly.

THE EDITORS

SOIL SCIENCE

VOLUME 73

May 1952

NUMBER 5

ESTIMATING THE INTEGRATED SOIL MOISTURE TENSION IN THE ROOT ZONE OF GROWING CROPS

STERLING A. TAYLOR

Utah Agricultural Experiment Station¹

Received for publication September 4, 1951

Because of the very low rate of movement of water in unsaturated soils, such soils cannot be maintained for long periods at constant moisture content in the range of availability to growing plants (3, 4, 8). It is necessary, therefore, to control moisture by letting the soil dry under natural growing conditions and then apply sufficient water to bring the profile to the upper limit of field moisture. Different moisture regimes are obtained by allowing some soils to dry to lower moisture contents and to lower depths than others before water is applied.

Several devices for measuring soil moisture have been used to indicate the moisture status of the soil and to indicate when water should be applied in the different moisture regimes. Tensiometers are useful to indicate soil moisture tension and relative moisture content in moist soils. Russell, Davis, and Bair (5) used tensiometers at various depths for following soil moisture conditions under corn. Haddock and Kelley (1, 2) have used both tensiometers and plaster blocks for following moisture conditions under sugar beets. These investigators presented their moisture data graphically showing the changes of tension or ohms resistance as functions of time.

The type of curve frequently presented is shown in figure 1, which indicates the changes of soil moisture tension with time during the growing season. Curves are frequently plotted with log resistance of plaster blocks as ordinate. Regardless of the units used to show moisture tension, the resulting curves are similar. As the soil dries out, the tension increases to some predetermined value, then irrigation water is applied and the tension drops quickly to a low value. On wetter soils the magnitude of the fluctuations is smaller, the dryer plots are at low tension values for a shorter period and are at high tension values for longer periods.

In addition to the time relationships, moisture data are frequently available for several depths in the profile. Figure 2 shows a series of moisture tension curves at various depths for several different times during the irrigation interval. The difficulty of interpreting such variable moisture relationships with crop yield, quality indexes, and water requirements is immediately apparent. It is

¹ Research supported by Regional Research Project W-9 with eleven western states, Soil Conservation Service, and Bureau of Plant Industry, Soils, and Agricultural Engineering cooperating.

the objective of this paper to present a method whereby these moisture data may be condensed and presented in such a form as to represent a single value that will

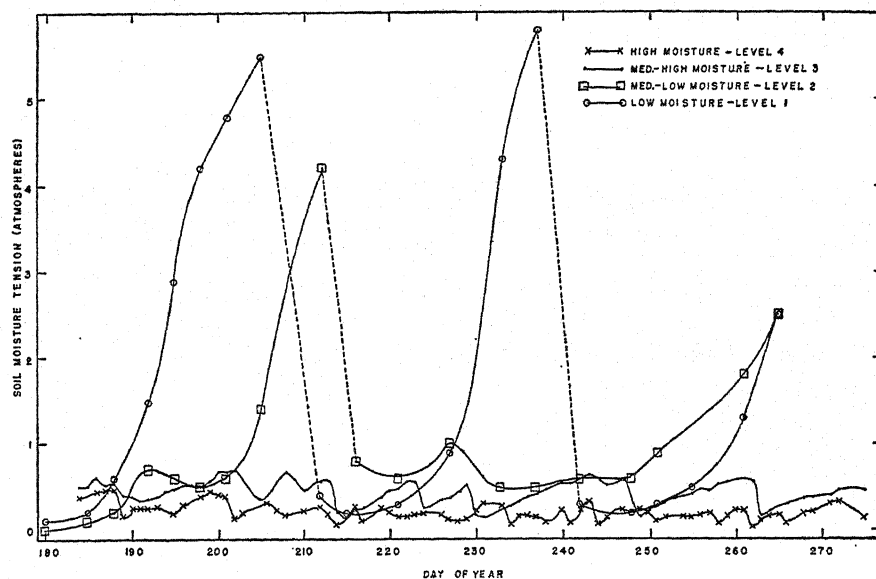


FIG. 1. PERIODIC CHANGES OF SOIL MOISTURE TENSION AT THE 12-INCH DEPTH FOR FOUR SOIL MOISTURE REGIMES DURING THE GROWING SEASON

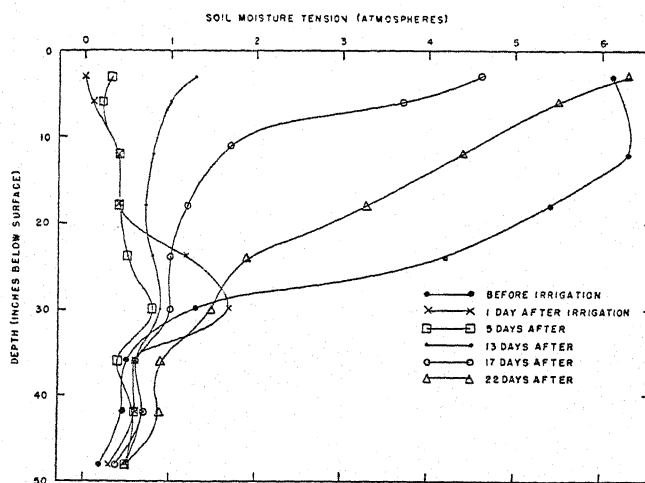


FIG. 2. SOIL MOISTURE TENSION AS A FUNCTION OF DEPTH AT VARIOUS INTERVALS BETWEEN IRRIGATIONS

express both the time and depth variations of moisture tension in a single field or plot planted to a given crop in any season.

THEORETICAL

Soil moisture tension is a continuous function of both depth and time, which can be expressed as:

$$T = f(x, t) \quad (1)$$

where x represents depth below the soil surface and t represents time. This functional relationship is very difficult to establish in terms of both variables, but for many environmental conditions it can be approximated rather closely.

Consider the relationship of tension and depth at any given time. The experimental curves in figure 2 include a family of curves that is fairly representative of observed relationships. It is possible to write a generalized equation for these curves expressing the tension, T , as a polynomial in x , then we can express the tension T_i at time i by the equation

$$T_i = a_0 + a_1x + a_2x^2 + \dots + a_nx^n \quad (2)$$

where a_1, a_2, \dots, a_n are time-dependent parameters and measure implicitly such variables as soil structure, evaporation rate, transpiration rate, kind of crop, depth of rooting, and season of year.

We will now consider the functional relationship of moisture tension and time at any predetermined depth. Examples from experimental data, of curves relating these two variables at the constant depth of 12 inches are given in figure 1. The tension at a given depth during the cycle between irrigation applications T_i can be represented by a functional relationship of the kind

$$T_i = f(t) = b_{0,i} + b_{1,i}t + b_{2,i}t^2 \cdots + b_{k,i}t^k \quad (3)$$

where the depth-dependent parameters b_0, b_1, \dots, b_k also depend on environmental conditions. Equations (2) and (3) can be combined to give a general functional relationship, if we note by observation that the parameters a_1, a_2, \dots, a_n of equation (2) are each continuous functions of time. The relationships can be expressed as polynomials.

$$\begin{aligned} a_0 &= P_0(t) = b_{00} + b_{01}t + \cdots b_{0k}t^k \\ a_1 &= P_1(t) = b_{10} + b_{11}t + \cdots b_{1k}t^k \\ &\dots\dots\dots \\ &\dots\dots\dots \\ &\dots\dots\dots \\ a_n &= P_n(t) = b_{n0} + b_{n1}t + \cdots b_{nk}t^k \end{aligned} \tag{4}$$

wherein $b_{00}, b_{01} \dots b_{nk}$ are parameters to be determined and $P_0(t) \dots P_n(t)$ represent polynomials in t . The moisture at any given depth and at any given time is then, from equation (2) and (4),

$$T_{ij} = P_0(t) + P_1(t)x + \dots + P_n(t)x^n \quad (5)$$

The integrated soil moisture tension in the root zone is then the double integral of equation (5) for both depth and time and can be represented by the equation

$$T_r = \int_{t_0}^{t_1} \int_{x=d_0}^{x=d} T_{ij} dx dt \quad (6)$$

where d_0 is the depth at the surface of the soil and d is the depth of the root zone, t_0 is the beginning time of the chosen interval, which may be the growing season, and t_1 is the end.

The equation can first be integrated with respect to depth, giving

$$\begin{aligned} T_r &= \int_{t_0}^{t_1} P_0(t)(d - d_0) dt + \int_{t_0}^{t_1} \frac{P_1(t)}{2} (d^2 - d_0^2) dt \\ &\quad + \dots + \int_{t_0}^{t_1} \frac{P_n(t)}{n+1} (d^{n+1} - d_0^{n+1}) dt \\ &= \sum_{i=0}^n \int_{t_0}^{t_1} \frac{P_i(t)}{i+1} (d^{i+1} - d_0^{i+1}) dt \end{aligned} \quad (7)$$

The second integration can be carried out with respect to time, giving the equation

$$\begin{aligned} T_r &= b_{00}(t_1 - t_0) + \frac{b_{01}}{2}(t_1^2 - t_0^2) + \dots + \frac{b_{0k}}{k+1}(t_1^{k+1} - t_0^{k+1}) \frac{d - d_0}{1} \\ &\quad + b_{10}(t_1 - t_0) + \frac{b_{11}}{2}(t_1^2 - t_0^2) + \dots + \frac{b_{1k}}{k+1}(t_1^{k+1} - t_0^{k+1}) \frac{d^2 - d_0^2}{2} \\ &\quad + \vdots \quad \quad \quad \vdots \quad \quad \quad \vdots \\ &\quad + b_{n0}(t_1 - t_0) + \frac{b_{n1}}{2}(t_1^2 - t_0^2) + \dots + \frac{b_{nk}}{k+1}(t_1^{k+1} - t_0^{k+1}) \frac{d^{n+1} - d_0^{n+1}}{n+1} \end{aligned} \quad (8)$$

or

$$T_r = \sum_{j=0}^k \sum_{i=0}^n \frac{b_{ij}}{j+1} (t_1^{j+1} - t_0^{j+1}) \frac{d^{i+1} - d_0^{i+1}}{i+1}$$

where i and j are integers and n and k represent the degree of the polynomial in x and t respectively.

APPROXIMATE METHOD FOR FIELD USE

In application it is not easy to find the best polynomial in x and t to fit the experimental data. Once this polynomial has been found and the coefficients have been determined, the integration is simply performed. The finding of these polynomials, their coefficients, and their integration form the basis of another investigation.

If we assume as a first approximation that tension is linearly related to depth and to time, then a polynomial of first degree will fit the data, and equation (8) will become

$$\begin{aligned} T_r &= b_{00}(t_1 - t_0)(d - d_0) + \frac{b_{01}}{2}(t_1^2 - t_0^2)(d - d_0) \\ &\quad + b_{10}(t_1 - t_0) \frac{(d^2 - d_0^2)}{2} + \frac{b_{11}(t_1^2 - t_0^2)(d^2 - d_0^2)}{4} \end{aligned} \quad (9)$$

The coefficients of $(d-d_0)$ and of $(d^2-d_0^2)$ are given in equation (4) as the parameters a_0 and a_1 of equation (2), and the coefficients of (t_1-t_0) and $(t_1^2-t_0^2)$, when considered independently of depth, give the coefficients b_0 and b_1 of equation (3). Equation (9) therefore reduces to the equation

$$T_p = \sum_{i=0}^m \sum_{j=0}^l T_{ij} \quad (10)$$

where l and m represent the number of depths and the number of times, respectively, that readings are made, and i and j represent a single time and a single depth. T_{ij} is then the moisture tension at a single time and a single depth, and T_p is the total moisture tension.

In applying this equation, it is then necessary to take readings at a series of depths and at various times throughout the season. In deriving equation (10) it was assumed that measurements were made at equal intervals of both depth and time. Since moisture-measuring devices are usually installed in the soil before the growing season begins, it is not difficult to space them equally with depth. In some cases, however, it might be desirable to space them unequally with depth to compensate for unequal root distribution. Weather conditions and other factors may make it impossible to take readings at equally spaced time intervals. To adjust for this discrepancy, a correction must be applied to (10) as follows:

$$T_p = \sum_{i=1}^m \sum_{j=0}^l (d_{i+1} - d_i) T_{ij} \quad (11)$$

where d represents the day of the year based on January 1 as day 1.

Frequently moisture devices are placed in the soil at intervals to greater depths than that to which the roots extend. This is necessary because roots extend deeper into the soil as the season progresses. If we assume that the moisture tension in the soil below the root zone of the plant will increase at only a very slow rate after it has reached the value it will have at the upper limit of available water, which is equivalent to the assumption that a discrete value exists for field capacity, furthermore, if the tension readings are or can be made uniform and constant at a value T_e on all devices measuring moisture at the upper limit of availability, and if we further define our reference point for zero tension at this value T_e , then we can write the integrated moisture tension in the root zone as

$$T_r = T_p - lT_e \quad (12)$$

or for the weighted case

$$T_r = T_p lT_e \sum_{i=0}^m (d_{i+1} - d_i)$$

The mean integrated soil moisture tension is obtained by dividing by the number of observations. For equal intervals we have

$$T_{pm} = \frac{\sum_{i=0}^m \sum_{j=0}^l T_{ij}}{ml} \quad (13)$$

and for the weighted case

$$T_{pm} = \frac{\sum_{i=0}^m \sum_{j=0}^l (d_{i+1} + d_i) T_{ij}}{l \sum_{i=0}^m (d_{i+1} - d_i)} \quad (14)$$

The mean integrated soil moisture tension in the root zone is

$$T_{rm} = T_{pm} - T_e \quad (15)$$

EXAMPLE FROM FIELD STUDY

In the field, measurements of soil moisture tension were taken at various depths in the profile and at various times during the irrigation season. At each time a continuous linear regression of tension on depth was calculated. The coefficients a_0 and a_1 of equation (2) along with the integration tension, the mean integrated tension, and the mean measured tension for each day are given in table 1. If we assume, as before, that the time dependence of tension can be approximated by a linear relationship, then it becomes necessary to calculate the linear regression of $a_0 a_1$ on time. This has been done, giving the following relationships for plot 114:

$$a_0 = 0.024 t + 1.79 \quad (16)$$

$$a_1 = 0.00052 t - 0.065$$

combining (16) and (5) after rearranging terms leads to

$$T_{ij} = 1.79 - 0.065 x + (0.024 + 0.00052 x) t \quad (17)$$

and the integrated soil moisture tension is

$$T_r = \int_3^{125} \int_{x=0}^{48} [1.79 - 0.065x + (0.024 + 0.00052x) t] dx dt \quad (18)$$

which gives, upon integration, $T_r = 14,952$ for all depth and for all times of the year. The mean integrated soil moisture tension representing the mean single observation at a single depth on any one day is obtained by dividing by the number of time intervals and depths represented. This value is $122 \times 48 = 5856$, and the mean integrated soil moisture tension for plot 114 is:

$$T_{rm} = 2.55 \quad (19)$$

Similarly for plot 118:

$$T_{rm} = 3.03 \quad (20)$$

These two values agree rather closely to the approximated values obtained by application of equation (13), which assumes equal time intervals between readings, and equation (14), which provides for a weighting factor to adjust the

TABLE 1

Integrated soil moisture tension in the root zone of growing sugar beets at various times after beginning of irrigation season

TIME AFTER BEGINNING OF SEASON days	LINEAR REGRESSION COEFFICIENT IN EQ. (2)		INTEGRATED MOISTURE TENSION		MEASURED MOISTURE TENSION MEAN
			Total	Mean	
	a_0	a_1	atm.	atm.	atm.

Plot 114					
3	1.27	+.002	65.6	1.37	1.32
19	0.28	+.006	20.4	0.42	0.30
28	0.44	+.001	22.3	0.46	0.46
33	0.76	-.003	33.0	0.69	0.67
37	1.21	-.014	42.8	0.89	0.87
40	1.43	-.021	44.4	0.93	0.92
46	3.76	-.088	79.1	1.64	1.62
48	4.34	-.100	93.1	1.94	1.91
52	4.21	-.084	105.3	2.19	2.17
55	5.27	-.098	140.1	2.92	2.88
58	6.66	-.129	171.1	3.56	3.53
61	7.59	-.148	193.8	4.04	3.99
65	8.10	-.150	216.0	4.51	4.46
72	2.49	+.011	132.2	2.75	2.76
76	2.00	+.015	113.3	2.36	2.36
81	2.01	+.017	116.2	2.42	2.42
87	4.48	-.045	163.2	3.40	3.39
93	7.95	-.104	261.8	5.45	5.42
97	8.77	-.101	304.6	6.35	6.32
102	1.87	+.084	186.5	3.89	3.91
107	0.27	+.107	136.2	2.84	2.87
111	1.97	+.057	160.2	3.34	3.36
115	1.26	+.052	120.4	2.51	2.52
121	3.04	+.038	189.7	3.95	3.96
125	4.86	+.003	236.7	4.93	4.93

Plot 118					
3	1.40	-.006	74.1	1.54	1.38
19	0.26	+.002	10.2	0.21	0.24
28	0.37	+.005	23.5	0.49	0.50
33	1.60	-.025	44.5	0.93	0.92
37	3.07	-.068	69.0	1.44	1.42
40	4.79	-.114	98.6	2.05	2.02
46	6.05	-.145	123.4	2.57	2.53
48	1.67	-.024	52.3	1.09	1.09
52	0.54	+.011	38.4	0.80	0.81
55	1.58	-.004	71.0	1.48	1.48
58	3.10	-.043	99.4	2.07	2.06
61	5.43	-.101	144.5	3.01	2.98
65	7.97	-.177	178.6	3.72	3.67
72	7.17	-.111	216.5	4.51	4.49
76	4.55	-.028	186.2	3.88	3.87
81	7.51	-.087	260.2	5.42	5.40
87	8.30	-.066	322.6	6.72	6.70
93	1.25	+.110	186.7	3.89	4.02
97	2.88	+.028	170.4	3.55	3.56
102	4.48	+.001	216.0	4.50	4.50
107	5.34	-.002	253.9	5.29	5.29
111	6.48	-.021	287.0	5.98	5.97
115	4.26	+.034	243.8	5.08	5.09
121	6.10	-.003	289.4	6.03	6.03
125	5.76	+.005	282.2	5.81	5.88

unequal time intervals. These comparisons of the three values for the two cases considered here are as follows:

MEAN INTEGRATED SOIL MOISTURE TENSION BY EQ. (6)	MEAN SOIL MOISTURE TENSION APPROX. BY EQ. (13)	MEAN WEIGHTED SOIL MOISTURE TENSION APPROX. BY EQ. (14)
2.55	2.78	2.48
3.03	3.28	3.18

It can be readily seen that the mean integrated values agree for these two cases within 9 per cent with the mean weighted values. This indicates that the approximate solution when weighted for time is sufficiently accurate for most applications.

DISCUSSION

In applying the theory proposed in this paper it is necessary to find polynomials that will fit the curves indicated in figures 1 and 2. These curves are constantly changing in a manner that depends on weather conditions, crop, depth of rooting, season, and soil.

The possibility of representing the data shown in figure 1 by a fourier series was abandoned for three reasons: First, the period between maximum tension is not uniform but is shorter during the hot summer months when crops are growing rapidly. Second, the maximum tension is not always the same but may vary somewhat as a result of inability to apply irrigation water at the exact time it should be applied. The second reason is more apparent in the higher moisture levels (that is, low tension levels), and the first, in the lower moisture levels as shown by figure 1. Third, the functional relationship is not uniquely defined at all times and at all depths but changes as roots penetrate into the soil to greater depths.

In practice the soil is often allowed to dry to some predetermined value of tension, at which time water is applied rapidly until the soil reaches its field-water-holding capacity. This value occurs at a tension that is very nearly constant for a single soil, and the error introduced by considering it to be a unique value is not great. Under such conditions a linear relationship between tension and time would not be greatly in error. The curves of figure 1 indicate that the error in assuming a linear relationship for moisture levels 4 and 3 is small. The error is somewhat larger in levels 1 and 2, however.

It appears that a third or fourth order polynomial would describe tension as a function of depth at any time, although at some times a fifth order polynomial may be required. As a first approximation the linear case has been used.

The application of this technique to field studies has been reported (6). It should be pointed out that the methods now in use for measuring soil moisture tension in the field are not completely satisfactory, but that in no way invalidates the theory proposed herein. Attention is being given to improving the methods for the field evaluation of soil moisture tension.

The integrated soil moisture stress as proposed by Wadleigh (7) can be ob-

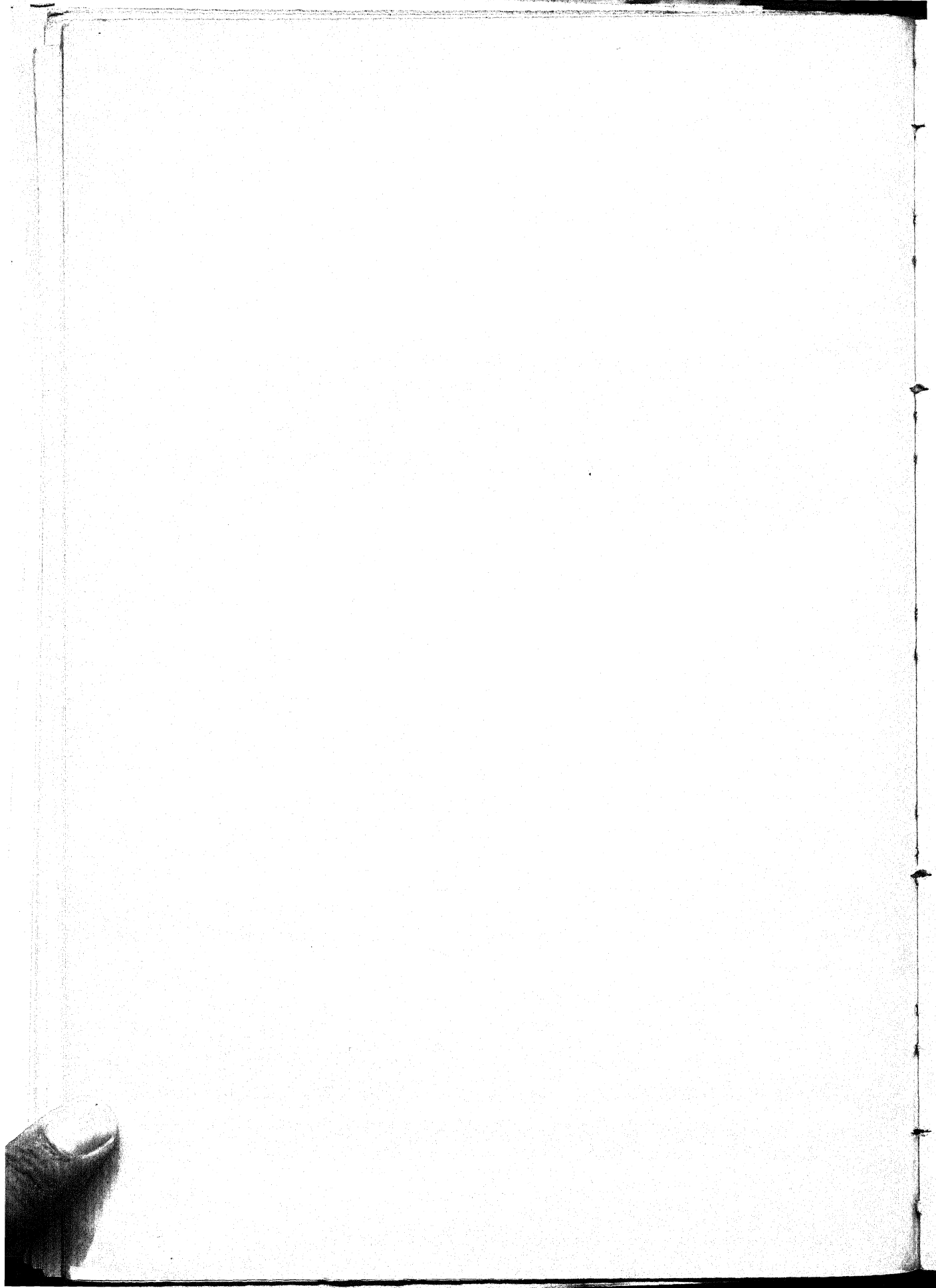
tained by measuring the osmotic pressure of the soil solution as a function of depth and moisture tension and adding it to equation (5) before integration. An approximation to the soil moisture stress can be had by first establishing the relationship of osmotic pressure to soil moisture tension at various depths for the soil in question, then integrating the pressure with depth and time and adding to the integrated tension. The relationship between osmotic pressure and tension can be calculated according to the relationship of Wadleigh: $\pi = 12Q/P_w$, where P_w is the percentage moisture in the sample, 12 in the percentage moisture at the time of displacement, Q is the osmotic pressure when $P_w = 12$. This assumes a linear relationship between osmotic concentration and moisture content. If this equation is valid, then the functional relationship between tension and osmotic pressure can be calculated from a single measurement of osmotic pressure at any known moisture content and the corresponding moisture release curve.

SUMMARY

A theory for integrating the soil moisture tension in the root zone of growing plants is presented. The application of the theory to field data has been accomplished by statistically fitting linear regression curves to large numbers of moisture tension readings taken at different depths in the root zone and at different times during the growing season. The equations of these curves are then integrated into a single value that approximates the true solution. This solution has been compared to a more easily obtained approximate solution obtained by assuming linear uniform relationships, then weighting the observations to adjust for unequal time intervals, adding, and taking the mean value. The error introduced by adding numbers as an approximation to an integration is shown to be small. The approximate solution is therefore considered to be adequate for many applications.

REFERENCES

- (1) HADDOCK, J. L., AND KELLEY, O. J. 1948 Interrelation of moisture, spacing and fertility to sugar beet production. *Amer. Soc. Sugar Beet Tech. Proc.* 1948: 378-396.
- (2) HADDOCK, J. L. 1949 Influence of plant population, soil moisture, and nitrogen fertilization on the sugar content and yield of sugar beets. *Agron. Jour.* 41: 79-84.
- (3) RICHARDS, L. A. 1941 Uptake and retention of water by soil as determined by distance to a water table. *Jour. Amer. Soc. Agron.* 33: 778-786.
- (4) RICHARDS, L. A., AND LOOMIS, W. E. 1942 Limitations of auto-irrigators for controlling soil moisture under growing plants. *Plant Physiol.* 17: 223-235.
- (5) RUSSELL, M. B., DAVIS, F. E., AND BAIR, R. A. 1940 Use of tensiometers for following soil moisture conditions under corn. *Jour. Amer. Soc. Agron.* 32: 922-930.
- (6) TAYLOR, S. A. 1951 Use of mean soil moisture tension to evaluate the effect of soil moisture on crop yields. *Soil Sci.* (in press).
- (7) WADLEIGH, C. H. 1946 Integrated soil moisture stress upon a root system in a large container of saline soil. *Soil Sci.* 61: 225-238.
- (8) WILSON, B. D., AND RICHARDS, S. J. 1938 Capillary conductivity of peat soils at different capillary tensions. *Jour. Amer. Soc. Agron.* 30: 583-588.



USE OF DITHIZONE AS AN EXTRACTANT TO ESTIMATE THE ZINC NUTRIENT STATUS OF SOILS

ELLSWORTH SHAW AND L. A. DEAN¹

U. S. Department of Agriculture

Received for publication August 23, 1951

The occurrence and recognition of zinc-deficiency symptoms in plants has stimulated much interest in the capacity of soils to supply zinc. During the last decade several different methods have been used for estimating this property of soils. A chemical test to determine the capacity of soils to supply zinc to plants will depend upon the extraction of a fraction of the soil zinc. Hibbard (4) working with California soils investigated the possibilities of making such an extraction, using both percolation and equilibrium methods, with different acids and salt solutions. The equilibrium method with KCl solution acidified to pH 3.2 was selected as the best of those tried. Thorne *et al.* (12) found this method to have no advantage over total zinc analysis.

Lyman and Dean (8) found a relationship between the amount of zinc extracted with normal ammonium acetate acidified to pH 4.6 from acid soils of Hawaii and the severity of zinc-deficiency symptoms on pineapple plants. Wear and Sommer (13) found a correlation between the occurrence of zinc-deficiency symptoms and the amount of zinc extracted with 0.04 *N* acetic acid and 0.1 *N* HCl from acid soils of Alabama. Epstein and Stout (3) extracted zinc from dilute clay suspensions with dithizone.

All of these methods are unsatisfactory for neutral and calcareous soils. None of the methods have been calibrated against a wide variety of soils. In the study reported here, approximately fifty different soils were used. These soils differed in pH, organic matter, clay, and total zinc content. Zinc was extracted directly from these samples with a two-phase system of aqueous ammonium acetate and CCl₄ containing dithizone. The amounts of zinc extracted have been correlated with the incidence of zinc-deficiency symptoms observed on plants in the field.

The particular method described has some theoretical advantages over others. Dithizone is a reagent which should effectively complex zinc cations in soils and solutions under ordinary pH conditions. The concentration of the zinc-dithizone complex in the aqueous ammonium acetate phase during extraction of zinc from the soil is kept low by adding CCl₄ and taking advantage of its greater solvent capacity. Thus the effect of adding a small volume of CCl₄ is equivalent to that of adding a large amount of aqueous extractant.

The accumulation of the extracted zinc in the organic phase results in another advantage. As CCl₄ is not absorbed by the wetted soil, a clean separation of the extracted zinc and soil can be effected by a pipetting operation. Furthermore,

¹ This investigation was supported in part by the U. S. Atomic Energy Commission. The authors wish to express their appreciation to F. G. Viets, J. I. Wear, W. Reuther, and H. V. Jordan for the soil samples used in preparing figure 1.

the glassware and reagents used in the extraction procedure are essentially those used for the final quantitative determination of zinc. Although other heavy metals form complexes with dithizone (9), interference from this source is prevented by the analytical method employed for the final zinc determination. The procedure for extraction with dithizone is not necessarily limited to zinc. The possibility of adapting this method to study other heavy metals occurring in soils is suggested.

REAGENTS AND SOIL SAMPLES

Carbon tetrachloride, c.p.—A.C.S. purity.

Sodium diethyldithiocarbamate, Eastman Kodak Co. (carbamate solution). Dissolve 0.2 gm. in 100 ml. zinc-free water. Prepare daily.

Diphenylthiocarbazone, Eastman Kodak Co. (dithizone solution). Prepare 0.01 per cent solution as follows: Dissolve 0.2 gm. in 1 liter CCl_4 . Shake frequently in a 4-liter separatory funnel for 15 minutes. Add 2 liters zinc-free 0.02 N NH_4OH (20 ml. of 1.0 N per liter), and shake to transfer dithizone to aqueous phase. Discard the CCl_4 (light green color) and rinse the aqueous phase with several 100-ml. portions of CCl_4 . Add 500 ml. of CCl_4 and 50 ml. 1 N zinc-free HCl . Shake to transfer dithizone to CCl_4 . Dilute CCl_4 -dithizone phase to 2 liters. Keep in glass-stoppered pyrex bottle stored in a refrigerator.

Ammonium acetate buffer (1 N solution). Add 77 gm. c.p. ammonium acetate to enough redistilled water to make a final volume of 1 liter. Adjust pH to 7 with zinc-free NH_4OH . Purify in a large separatory funnel with dithizone and CCl_4 , discarding organic phase until it no longer changes color. Remove dithizone dissolved in aqueous phase by repeated extractions with CCl_4 .

Ammonium citrate buffer (0.4 M solution). Add 90 gm. dibasic ammonium citrate to enough water to make 1 liter. Add concentrated zinc-free NH_4OH until pH is 8.5. Purify with dithizone and CCl_4 as previously described.

Hydrochloric acid (1 N solution). Distill a 1:1 mixture of HCl and distilled water in a pyrex glass still. Dilute condensate from constant boiling mixture to 1 N with zinc-free water.

Ammonium hydroxide (1 N solution). Distill concentrated NH_4OH into zinc-free water in pyrex container immersed in an ice bath. Zinc-free NH_4OH may also be prepared by collecting anhydrous ammonia in a pyrex container of zinc-free water.

Zinc-free water. Redistill water in all-glass pyrex still, or pass distilled water through ion-exchange column.

Standard zinc solution (100 ppm.). Dissolve 0.1 gm. pure zinc in 50 ml. 0.02 N H_2SO_4 . Dilute to 1 liter.

Since the quantities of zinc extracted are very small, the soil samples must be collected and prepared with the usual care recommended for minor-element work. The soils should be air-dried, crushed with a wooden pestle, and passed through a zinc-free 18-mesh sieve. The screening of soils should be done with iron or any zinc-free wire (commercially available). Samples may be conveniently stored in cardboard ice cream containers. All of the brands of cleansing tissue examined have been sufficiently free of zinc to be useful for such operations as wiping out weighing pans.

EXTRACTION PROCEDURE

The method of extracting zinc from soils with the aid of dithizone is as follows: Pipette 25 ml. of ammonium acetate solution and 25 ml. of dithizone- CCl_4 solu-

tion into a 125-ml. Squibb pear-shaped separatory funnel. Add 2.5 gm. of soil of such particle size as to pass an 18-mesh sieve. Firmly seat stopper and shake funnels on mechanical shaker (6) for 1 hour. Replace separatory funnels in stand and drain each soil- CCl_4 suspension into a 40-ml. conical centrifuge tube. Centrifuge contents to develop a continuous CCl_4 phase. Take a 10-ml. aliquot of this phase with a pipette. The practice of using a hand pipettor is recommended because the operator needs to see and correctly locate the tip of the pipette in the organic phase. Air should be expelled as the tip is passed through the aqueous and soil layers, and the tip must be kept away from the walls of the tube where soil and water may be contacted. (A mark on the pipette will greatly facilitate placing the pipette at the proper depth.) Withdraw the pipette and rinse the adhering soil and water from the tip using a wash bottle; adjust to mark, and rinse again. Add the aliquot to the clean separatory funnel from which it originally came and which was cleaned by rinsing with water while the samples were being centrifuged. Add 50 ml. of 0.02 *N* HCl and extract on shaker for 3 minutes. Discard the CCl_4 phase, which contains interfering elements and some oxidized dithizone. Rinse the aqueous phase twice with CCl_4 , shaking by hand. From this point, the analysis may be continued with any of the standard methods for determining zinc on an aqueous solution.

In this laboratory the zinc is colorimetrically determined by the method of Cowling and Miller (2) as modified by Holmes (5).

Add 1 drop phenolphthalein indicator, 5 ml. ammonium citrate buffer, 1.1 ml. *N* NH_4OH , 5 ml. carbamate, and exactly 10 ml. of dithizone reagent. Extract on shaker for 5 minutes, and transfer organic phase to another separatory funnel. Add 25 ml. 0.01 *N* NH_4OH , and extract again for 3 minutes. Take a 5-ml. aliquot of the organic phase with a pipette, and dilute with CCl_4 to 25 ml. Transfer to a colorimeter and measure the transmission of light having a wavelength of approximately 5350 Å. Calculate the amount of zinc present by comparing with a standard curve prepared in an identical manner for known amounts of zinc. All equipment may be satisfactorily cleaned by rinsing with either CCl_4 or water if its use is restricted to this analysis. Further improvements on the original method for determining zinc have been reported (9, 10, 11).

FACTORS INFLUENCING EXTRACTION

A variety of soil types was used in the development of this method and in testing its applicability. At the outset it was necessary to determine the effect of time on the completeness of extraction. The effect of varying time is shown in table 1.

In the 10-minute period about half as much zinc was extracted as during the longer periods. The 2-hour period had no advantage over the 1-hour period to compensate for the extra time. The 1-hour extraction period was selected because of the relatively large amount of zinc extracted and the slight effect of minor variations in time. The values in the table are averages of six determinations, from which the standard errors were calculated. The magnitude of the standard error seems to be a property of the soil, possibly the homogeneity of the sample.

The 2-hour extraction of the Palouse soil removed less zinc than the 1-hour. The cause of this decrease was not investigated. The amount of zinc extracted by dithizone was not found to be correlated with the total amount of zinc present in the soil.

Another group of soils was used to measure the effect of the pH level of the aqueous phase on the amount of zinc extracted. This effect was examined by means of the regular method with dithizone and also by a modified method without dithizone. The modification consisted of extraction in the regular manner but omitting the dithizone- CCl_4 reagent. The soil suspension was centrifuged and an aliquot taken from the clear supernatant liquid. This aliquot was tested

TABLE 1
Effect of time of extraction on amount of zinc extracted by dithizone from soil

SAMPLE NO.	SOIL	ZINC EXTRACTED DURING SHAKING PERIODS		
		10 Minutes	1 Hour	2 Hours
		<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>
6797	Shelby silt loam	3.27 \pm .61	4.19 \pm .37	3.95 \pm .59
6843	Colby silty clay loam	1.93 \pm .18	3.55 \pm .14	3.71 \pm .13
6096	Houston clay	2.74 \pm .43	5.90 \pm .86	6.22 \pm .45
8069	Palouse silt loam	2.75 \pm .27	5.73 \pm .26	4.96 \pm .11
C7190	Norfolk sandy loam	2.39 \pm .16	3.85 \pm .07	4.17 \pm .11
C7173	Cecil fine sandy loam	0.58 \pm .05	0.98 \pm .02	1.17 \pm .03

TABLE 2
Effect of dithizone at different pH values on extraction of zinc from soils

CONDITION	ZINC EXTRACTED			
	50333 Davidson	50354 Glenelg	50351 Frankstown	50348 Myersville
	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>
Ammonium acetate at pH 7 with dithizone.....	4.3	12.7	1.1	0.6
Ammonium acetate at pH 7.....	0.0	1.0	0.0	0.0
Ammonium acetate at pH 8.5 with dithizone....	4.0	11.6	1.2	0.5
Ammonium acetate at pH 8.5.....	0.0	0.5	0.0	0.0
0.1 N Acetic acid.....	1.5	8.0	—	0.4

for zinc by the previously described method for determining zinc in aqueous solutions. The results are shown in table 2.

In absence of the dithizone- CCl_4 phase, the ammonium acetate extracts little or no zinc from soils under these pH conditions. The amounts extracted at the two different pH values are similar, indicating the noncritical effect of pH within the range examined. The 0.1 N acetic acid is shown to indicate the relative extracting power of acetic acid and dithizone. On the basis of these findings, normal ammonium acetate buffer at pH 7 was selected.

The procedures for obtaining and preparing soil samples for laboratory determinations influence the properties determined. The common arbitrary practice, based on classification of soil separates for mechanical analysis, is to determine

chemical properties on that fraction of the soil which passes a sieve with openings 2 mm. in diameter. In the method used here zinc is extracted from that fraction of the soil which passes a sieve with 1-mm. openings. This practice was adopted because soil particles as large as 2 mm. in diameter will not pass the stopcock bore of ordinary separatory funnels. Neglecting the weight of very fine gravel in the calculation of the amount of zinc extracted in terms of parts per million soil introduces no serious error, because the fraction discarded is usually small.

Consideration was given to methods for preparing suitable soil samples. Grinding the soil makes it possible to obtain small subsamples which are homogeneous and representative of the entire sample. Since grinding exposes new surfaces that might shift soil equilibria, a comparison was made of the amounts of zinc extracted from samples ground to three different sizes. Soil samples were first screened to pass a 2-mm. sieve, the clods being broken by a wooden pestle. This sample was then further reduced with a wooden pestle and light pressure to pass an 18-mesh sieve (fraction 1). Portions of this material were then ground by hand in a mullite mortar, and samples were selected from that soil which

TABLE 3
Effect of grinding on amount of zinc extracted from soils

SAMPLE NO.	SOIL	ZINC EXTRACTED		
		Fraction 1, sieved to pass 18-mesh	Fraction 2, ground by hand to pass 60-mesh	Fraction 3, ground by hand to pass 200-mesh
		<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>
50333	Davidson clay loam	3.4	4.3	5.5
50354	Glenelg loam	10.3	12.8	14.9
50348	Myersville silt loam	0.2	0.2	0.6

passed 60- and 200-mesh bolting cloth (fractions 2 and 3, respectively). The amounts of zinc extracted from equal weights of these samples which received different amounts of grinding are shown in table 3.

Grinding increased the amount of zinc extracted from the soils. An increase of approximately 25 per cent was effected by reducing the soil to <60-mesh. This increase was considered to be the result of exposure of new mineral surfaces and was large enough to be considered undesirable. Mechanical preparation of the sample was therefore limited to breaking aggregates with a wooden pestle and passing the soil through an 18-mesh sieve.

There is general agreement that organic matter in soils affects the availability of minor elements. The presence of organic matter is thought to contribute to deficiency conditions in some instances and to alleviate them in other instances. Experiments were conducted to find what effect the destruction of organic matter in soil would have on the amount of zinc extracted by dithizone. Use of H_2O_2 to oxidize the organic matter is unsatisfactory because of the effect on the mineral fraction of the sample. Therefore destruction of organic matter by dry heat was investigated.

A temperature of 300°C. maintained for 48 hours will destroy approximately 85 per cent of the organic matter, leaving a charred residue (7). Other reactions that affect the extraction of zinc might also occur. Table 4 shows that heating caused an appreciable increase in the amount of zinc extracted from some soils and little change in others.

The behavior of the Norfolk and Lakeland soils was typical of samples obtained from the southeast. The Sagemoor, Timmerman, and Ephrata represent soils of the Columbia Basin in Washington. The Williams of North Dakota like-

TABLE 4
Effect of heating at 300°C. for 48 hours on availability of zinc in different soils

SAMPLE NO.	SOIL	ZINC	
		Unheated	Heated
		<i>p.p.m.</i>	<i>p.p.m.</i>
51285	Sagemoor sandy loam	0.1	1.5
51290	Timmerman fine sandy loam	0.2	0.7
51288	Ephrata sandy loam	0.6	1.6
51256	Williams sandy loam	0.3	3.0
51250	Norfolk sandy loam	0.9	1.3
51272	Lakeland loamy sand	3.0	3.2

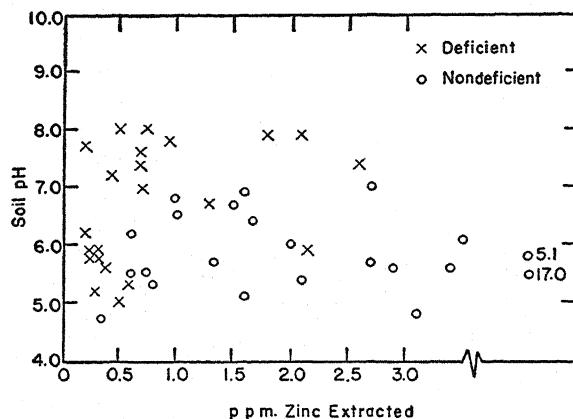


FIG. 1. pH AND EXTRACTABLE ZINC IN DEFICIENT AND NONDEFICIENT SOILS

wise showed a large increase. The mechanism for this increase has not yet been determined; nor is it established that the presence of organic matter is related to the effect of preheating.

COMPARISON OF RESULTS OF DITHIZONE METHOD AND PLANT INDICATIONS

The direct extraction of zinc with dithizone described in this paper has been used to test a wide variety of soils. Samples representing the surface to a depth of 6 to 12 inches were obtained from different regions where zinc deficiency occurs. These samples were classified on the basis of crop condition as soils that supported plants with or without zinc-deficiency symptoms, without regard to type of crop.

Figure 1 shows the amount of zinc extracted by the dithizone method plotted against the soil pH for both deficient and nondeficient soils.

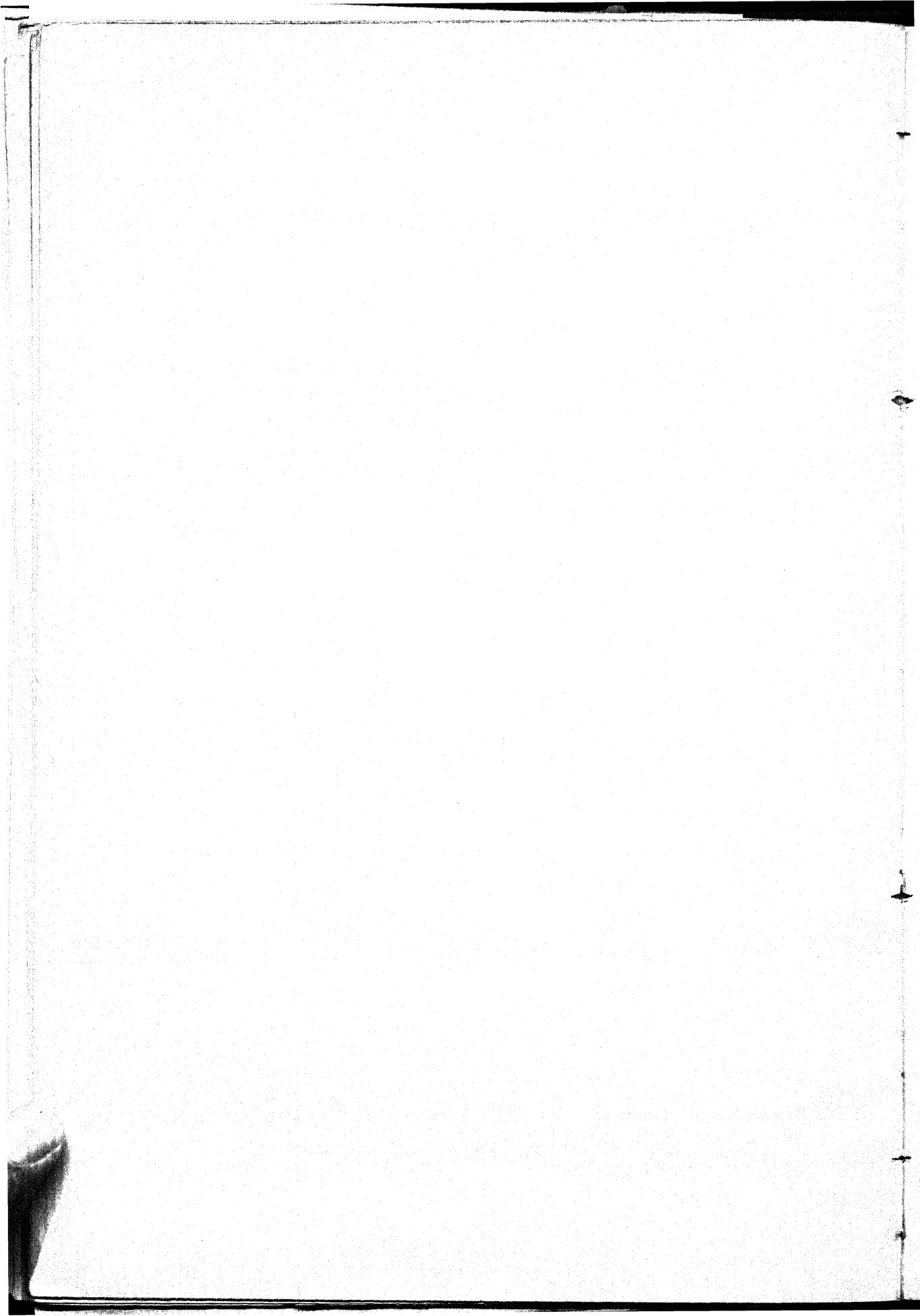
When the amount of zinc and the soil pH are both considered, it appears that deficiency symptoms occur on soils with a high pH when the amount of zinc present would be ample to prevent deficiency if the pH were lower. The higher pH apparently reduces the fraction of the soil zinc that is available to plants. Deficiency will occur on such soils unless compensated by presence of a greater amount of zinc. Figure 1 shows a high degree of segregation of the deficient and nondeficient soils which are representative of many zinc-deficient areas. This indicates that the dithizone method of extraction of soil zinc, combined with pH measurement, may be a useful procedure for predicting the capacity of any soil to supply plants adequately with zinc.

SUMMARY

A dithizone extraction procedure to measure available zinc in soils was investigated. Factors affecting the results, such as time of extraction, pH, and mechanical and thermal pretreatment were examined. Optimum conditions were selected, and the test was applied to soil samples representing many different soils from major areas of zinc deficiency in the United States. A scatter diagram of the results shows a relationship among soil pH, dithizone-extractable zinc, and the occurrence of plants with zinc-deficiency symptoms. On the basis of these data this procedure may be of value for indicating the zinc status of soils.

REFERENCES

- (1) COWLING, H. 1941 Report on zinc in plants. *Jour. Assoc. Off. Agr. Chem.* 24: 520-525.
- (2) COWLING, H., AND MILLER, E. J. 1941 Determination of small amounts of zinc in plant materials. *Indus. and Engin. Chem., Analyt. Ed.* 13: 145-149.
- (3) EPSTEIN, E., AND STOUT, P. R. 1951 The micronutrient cations iron, manganese, zinc, and copper: their uptake by plants from the adsorbed state. *Soil Sci.* 72: 47-66.
- (4) HIBBARD, P. L. 1940 Chemical status of zinc in the soil with methods of analysis. *Hilgardia* 13: 1-29.
- (5) HOLMES, R. S. 1945 Determination of total copper, zinc, cobalt, and lead in soils and soil solutions. *Soil Sci.* 59: 77-84.
- (6) HOLMES, R. S., AND MULLINS, J. F. 1950 A vertical shaker for separatory funnels. *Soil Sci.* 69: 233-237.
- (7) HOSKING, J. S. 1938 Ignition at low temperatures of the organic matter in soils. *Jour. Agr. Sci.* 28: Part 3.
- (8) LYMAN, C., AND DEAN, L. A. 1942 Zinc deficiency of pineapples in relation to soil and plant composition. *Soil Sci.* 54: 315-324.
- (9) SANDELL, E. B. 1944 Colorimetric Determination of Traces of Metals. Interscience Publishers, Inc., New York.
- (10) SHIRLEY, R. L., et al. 1948 Report on zinc in plants. *Jour. Assoc. Off. Agr. Chem.* 31: 285-293.
- (11) SHIRLEY, R. L., et al. 1949 Report on zinc in plants. *Jour. Assoc. Off. Agr. Chem.* 32: 276-280.
- (12) THORNE, D. W., LAWS, W. D., AND WALLACE, A. 1942 Zinc relationships of some Utah soils. *Soil Sci.* 54: 463-468.
- (13) WEAR, J. I., AND SOMMER, A. L. 1948 Acid-extractable zinc of soils in relation to the occurrence of zinc-deficiency symptoms of corn: a method of analysis. *Soil Sci. Soc. Amer. Proc.* (1947) 12: 143-144.



ORIGIN OF THE BASE-EXCHANGE CAPACITY OF CLAYS AND SIGNIFICANCE OF ITS UPPER LIMITING VALUE

R. P. MITRA AND K. S. RAJAGOPALAN

University of Delhi, India

Received for publication June 1, 1951

Although a considerable body of information concerning the many practical aspects of base exchange in clays is now available, such fundamental questions as to what is the base-exchange capacity really due, and whether it has any definite limiting value, still remain inadequately answered. The clay mineral concept developed during the last 20 years has focused attention on the origin of the base-exchange capacity of clays in relation to their lattice structures. Subsequently, the view was expressed (2, 4) and is now generally held that most of the exchangeable cations are such monovalent and bivalent cations of the clay lattice as balance negative charges caused by isomorphous replacements in the tetrahedral and octahedral layers of the lattice and are yet accessible to the cations of a "contact" solution. Limitations of this point of view are, however, recognized. It fails completely in kaolinite and kaolinitic clays where isomorphous replacement is rather the exception than the rule. And in illite or hydrous mica, also, the negative "isomorphous" charge has been found to fall short of its observed base-exchange capacity (2). Indeed, the realization has grown in recent years, among soil scientists and clay crystallographers, that some other source of the negative charge of clay crystals, responsible for their base-exchange capacity, exists.

This paper seeks to reveal the nature of this charge and define conditions under which the total negative charge of the surface will be operative and thus bring out the maximum possible value of the base-exchange or base-combining capacity.

ACID CHARACTER AND BASE-COMBINING POWER OF HYDROXYL GROUPS IN KAOLINITE

Kelley and Jenny (3) have expressed the view that kaolinite owes its base-exchange capacity to H ions dissociated from the available OH-groups of its crystal lattice. They have, however, brought no direct experimental evidence to bear on this view. On the other hand, the alternative suggestion has been made (2) that the base-exchange capacity of kaolinite arises from unsatisfied oxygen valences developed on the lateral surfaces of the crystals. No systematic attempt has been made to decide between these rival viewpoints by actual experiments or quite convincing arguments. Mitra (6) found two inflections in the titration curve of kaolinite. Mitra and Rajagopalan (7) attributed these inflections to the neutralization of H ions dissociated from the available OH-groups of the kaolinite lattice. Kaolinite has two types of OH-planes, one made up entirely of OH-groups and forming the exposed surface of a lattice packet, and the other, a composite (O, OH) plane imbedded within a hexagonal network of oxygen ions. As the

ionic environments of OH-groups belonging to these two types of OH-planes are not identical, their energies of dissociation might very well be different, thus giving the two inflections in the titration curve. For every three OH-groups belonging to the purely OH-plane, there is only one such group in the (O, OH) plane.

Mitra, however, found that the ratio of the base-exchange capacities at the two inflections was 2:1, and not 4:1 as one would expect if all the available OH-groups were neutralized at the final inflection. That this does not happen might be explained as follows: The two bounding (001) planes of each kaolinite crystal—one, a rather loosely packed oxygen plane, and the other, a closely packed plane of OH-groups—are, as a rule, widely separated from each other, inasmuch as the thinnest kaolinite crystal will be at least several unit cells thick. The OH-groups of the composite (O, OH) plane, which is situated immediately below the bounding oxygen plane, are available for interaction with a base through hexagonal rings of oxygens of the oxygen plane, and it is believed that the first inflection in the titration curve of kaolinite corresponds to the neutralization of these OH-groups. At a higher pH, one in every three OH-groups of the exposed OH-plane (the three OH-groups are attached to a single Al atom¹) is neutralized by the base, MeOH. The resulting OMe-group readily dissociates and, in so doing, imparts a negative charge to the Al atom with which the neutralized OH-group is coordinated. This negative charge is communicated to the oxygens of the two remaining OH-groups bonded to the Al atom, and this hampers their dissociation and neutralization by the base. The part of the titration curve between the first and second inflections thus corresponds to the neutralization of only one in every three OH-groups of the OH-plane. Neutralization of the two remaining OH-groups would require a very high pH, and under such extreme alkaline conditions hydrolytic effects would set in and mask the inflection point, as they do in the case of H ions belonging to the third stage of dissociation of phosphoric acid.

ACID CHARACTER OF HYDROXYL GROUPS IN MICAS AND OTHER LAYER-LATTICE SILICATES

Unequivocal evidence of the acid character of OH-groups in three-layer silicates has been obtained from studies of the titration curves of hydrogen mica prepared by leaching finely ground muscovite with dilute HCl to replace the exposed K ions of the mica crystals by H ions. The titration curves have been briefly reported elsewhere (8) and will be more fully discussed in a separate communication. Only information relevant to our discussion will be considered here. From a ground specimen of muscovite, 13.0 me. of K⁺ per 100 gm. was liberated on exhaustive treatment with dilute HCl. When the resulting hydrogen mica was potentiometrically titrated with KOH, it gave a titration curve with three inflections. The first was rather weak, but the other two were prominent

¹ This is not the same Al atom as the one to which the already neutralized OH-group of the (O, OH) plane is attached, since, as previously explained, the exposed (O, OH) and OH-planes are widely separated from each other.

and were found near pH 9.0 and 10.5. The titration curve in figure 1 shows these two prominent inflections, which indicated base-exchange capacities of 13.0 and 39.0 me., respectively, per 100 gm. of the hydrogen mica. The agreement between the base-exchange capacity corresponding to the second inflection and the

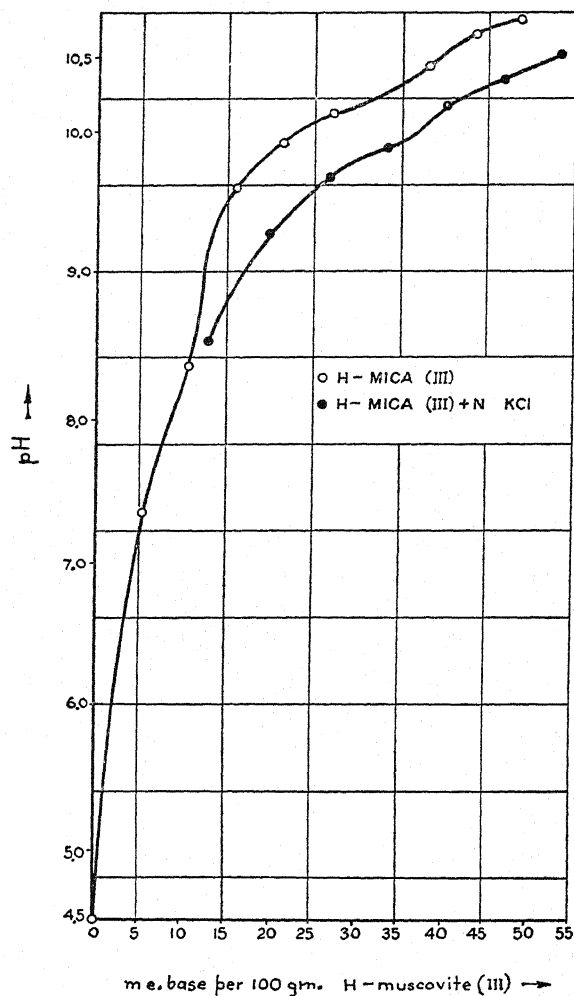


FIG. 1. TITRATION CURVES OF HYDROGEN MICA WITH KOH IN PRESENCE AND ABSENCE OF N KCl

quantity of displaced K^+ found in the HCl extract of the original mica shows that this inflection marks the completion of the neutralization of H ions acquired by the surfaces of the mica crystals in exchange for their exposed K ions. Such H ions are, of course, bonded to the surface by the negative charges arising from the isomorphous replacement of every fourth Si ion in the tetrahedral layer of the lattice by an Al ion. The base-exchange capacities calculated at the third

and second inflections are as 3:1. This is just what would be expected if the two OH-groups reckoned for each H ion of the above category in the hydrogen mica [to which the idealized formula, $\text{HAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ could be given] reacted with the base at the third, or final, inflection. Actually, for each H ion acquired in exchange for an exposed K ion, two structurally identical OH-groups are available for interaction with the base through hexagonal rings of oxygens. The part of the titration curve between the second and third inflections, therefore, indicates the neutralization of H ions dissociated from these OH-groups, and the third inflection marks the end point of this neutralization process.

If the OH-groups in hydrogen mica could react with a base in so unmistakable a manner, there seems to be no reason why they should not do so in clay crystals also. Hydrogen mica, of course, provides a standard against which the available OH-groups can be estimated. If the H ions that react with the base can be measured, the number of OH-groups that should also react can be calculated. As already mentioned, the titration curve of hydrogen mica shows an inflection that gives a measure of the H ions balancing the isomorphous charge. And the curve shows another inflection, the third and final one, that gives the calculated amount of OH-groups. It is not easy to make such a strict comparison between the isomorphous and hydroxylic charges of clay crystals, as in their case there is no criterion for distinguishing between the two types of charges. The necessary criterion does exist for muscovite, for there the isomorphous charge is given by the quantity of K ions which is exchanged for H ions in preparing the hydrogen mica. The clay minerals also give definite amounts of monovalent and bivalent cations on being leached with dilute mineral acids. But in their case, there is no *a priori* reason to say that so many of them balanced the isomorphous charge and so many, the charge of the other type, although it is fairly certain, in light of the work on hydrogen mica, that the total negative charge of the surface which is responsible for their maximum base-exchange, or base-combining, capacity is partly isomorphous and partly hydroxylic.

Schofield (11) has also referred to a possible hydroxylic charge of clay crystals without producing any conclusive experimental evidence for his views. He has even sought to distinguish between the isomorphous and hydroxylic charges on the basis of his belief that, unlike the charge of the latter type, the isomorphous charge is permanent in the sense that it is not a function of the pH whereas the hydroxylic charge is. It will be shown in the following section that no part of the total charge is "permanent" in the sense in which the term has been used by Schofield, and consequently the criterion laid down by him for distinguishing between the two types of charges cannot be depended upon. Incidentally, it is not quite clear which OH-groups Schofield had in mind when he discussed the hydroxylic charge. He spoke of "hydroxyl groups attached to silicons" and believed that they "must occur at the edges of silicon-oxygen sheets." According to the accepted structures of layer-lattice silicates, only cations in octahedral coordination have OH-groups attached. One, then, gets the impression that Schofield was not thinking of structural OH-groups when he mentioned the hydroxylic charge, but rather of OH-groups adventitiously acquired by the clay

crystals, for example, by adsorption. One could hardly believe that an accidentally acquired hydroxylic charge could bear such a constant relation to the isomorphous charge as it does in hydrogen mica.

In a recent paper, Hauser *et al.* (1) have reported some infrared absorption studies of clays which bring out absorption bands characteristic of OH-groups. They attributed the bands to adsorbed OH-groups. They seemed to lose sight of the fact that such structural OH-groups as are available might also be responsible for the bands. Indeed, this appears to be the real explanation of the bands, apart from the possibility that adsorbed water molecules rather than OH groups could also be a contributing factor, though this would be less likely in the nonswelling clays and extremely unlikely at temperatures higher than 200°C. Mention has too often been made of the adsorption of OH-groups by clay crystals without reference to the full implications of this type of adsorption. The balance of charges in the solid crystal would be obviously offset if adsorption of OH ions were not countered by a simultaneous adsorption of an equivalent amount of cations, which means that a whole molecule, say, of water or an alkali has to be adsorbed. If this molecule is assumed to remain in a state of dissociation on the surface, there is, of course, no inconsistency in the further assumption inherent in the discussions of Hauser *et al.* that the positively charged counter ions, which are either the H ions of water or the metal cations of an alkali, will be the exchangeable cations of the clay. The main criticism against this mechanism is that it would make the base-exchange or base-combining capacity an extremely ill-defined quantity which would progressively increase with the pH of the contact solution and would have no definite limiting value, such as would be indicated by an inflection in the titration curve. The fact remains that an inflection is obtained in all cases, and, at least for hydrogen mica, this inflection admits of a quantitative interpretation in terms of the activity of the structural OH-groups available on the surface. Electrochemistry of the clays, including base exchange, is undoubtedly a property of the surface, as Hauser *et al.* seek to emphasize, but the surface structure is deducible from the lattice structure and for mica deductions from the lattice structure are in complete accord with the observed surface chemical behavior.

Neutralization of H ions dissociated from the OH-groups of the (O, OH) planes imparts to the surface a negative charge, which is balanced by the cations of the base. These cations will be drawn as close to the center of the negative charge as possible. There is, at first, not much danger of the cation's going through the hexagonal ring of oxygens when it happens to be a small-sized cation like Na^+ or K^+ . If any credence is to be given to the idea of hydration of cations in solution, however, the hydrodynamic radii of even such cations as Na^+ and K^+ would be much too large to admit of their passage through the rings. On the other hand, the evidence obtained with hydrogen mica admits of little doubt that the OH-groups of the crystals do react with the base, as that seems to be the only plausible explanation of the constant ratio of 3:1 between the base-exchange capacities at the third and second inflections. One is then forced to conclude that the large hydrated cations do not go through the rings, but merely

crowd as close to them as possible, being drawn by the electrostatic attraction of the negative charge which the crystal acquires by removal of the H ions of its OH-groups as water after their neutralization with the OH ions of the base. There seems to be no other explanation in the case of bases having large cations, such as Ba^{++} . There is practically no chance of the Ba ions going through the rings even in the dehydrated condition, and yet the fact remains that under suitable conditions Ba ions are taken up by hydrogen mica in amounts equivalent to the base-exchange capacity at the third inflection in the titration curve with NaOH or KOH.

What really happens in this case also is that Ba ions are drawn as close to the crystal surface as possible by the electrostatic attraction of the neutralized sub-surface OH-groups of the crystal. Indeed, for bases having polyvalent cations, a situation is created which rules out the possibility of the cations' going through the oxygen rings even when they are small enough to do so. Obviously, each such cation has to balance the negative charge of an equivalent number of neutralized OH-groups. This it can do, not by trying to get at anyone of them through the superimposed hexagonal rings of the latter, but by taking up such a position on the exposed (001) plane that its positive charge is distributed equally among an equivalent number of negative centers created by the neutralization of the OH-groups of the crystal by the OH ions of the base.

BASE-EXCHANGE CAPACITY AS A FUNCTION OF CONDITIONS OF ESTIMATION AND REALIZATION OF UPPER LIMITING VALUE

The base-exchange reaction between a clay and a contact solution being essentially balanced, routine analytical methods of estimating the "total" exchange capacity aim at ensuring conditions which would favor a continuous shift in the equilibrium until the total quantity of exchangeable cation could be displaced and then estimated. Routine methods in vogue, however, seldom give concordant results (12). It is now known that the uncertainty arises mainly from the difficulty of an exact definition and unequivocal estimation of the so-called exchangeable hydrogen of the soil or clay. Mukherjee, Mitra, and their co-workers have shown (5, 9) that particularly important to such an estimation are the pH of the contact solution and the nature and concentration of the exchanging cations. The higher the equilibrium pH and the greater the concentration and the valency of the exchanging cation, the larger will be the quantity of H ions which will be exchanged. This raises the important question of whether a definite base-saturation limit of clays exists and, if so, what the significance of the limiting saturation capacity is. The authors believe that their work on hydrogen mica provides definite answers to both these questions, namely, that the negative charge of the surface that is responsible for the base-exchange capacity has a definite limiting value and that the total negative charge is partly isomorphous and partly hydroxylic. Furthermore, the total charge will be revealed by the final inflection in the titration curve of the hydrogen mineral with a base, provided secondary effects, such as decomposition of the clay, do not occur. Analytical methods of determining the base-exchange capacity which

depend on estimating the amount of cation taken up by a clay from solutions of salts will, as a rule, give results that will be too low in comparison with the total charge. Only in rather exceptional cases, when either the pH is sufficiently high

TABLE 1

Base-exchange capacities of hydrogen mica, hydrogen illite, and hydrogen kaolinite determined by different methods

SYSTEM	METHOD OF ESTIMATING BASE-EXCHANGE CAPACITY	pH OF SOLUTION	BASE-EXCHANGE CAPACITY <i>me./100 gm.</i>
Hydrogen mica	Potentiometric titration with KOH	7.25 (at second inflection)	13.0
		10.3 (at final inflection)	39.0
	Parker's method [leaching with N $Ba(Ac)_2$ and estimation of adsorbed Ba]	7.0	13.0
	Leaching with N $BaCl_2$ and estimation of adsorbed Ba	1.5	7.0
		6.0	9.5
		9.7	37.0
	Leaching with $8.5 N$ $Ba(SCN)_2$ and estimation of adsorbed Ba	7.2	31.0
		8.1	39.0
Hydrogen illite	Electrometric titration with KOH	7.6 (at second inflection)	20.0
		11.0 (at final inflection)	60.0
	Parker's method	7.0	42.0
	Leaching with N $Ba(SCN)_2$ and estimation of adsorbed Ba	7.2	44.0
	Leaching with $8.5 N$ $Ba(SCN)_2$ and estimation of adsorbed Ba	8.5	58.0
Hydrogen kaolinite	Electrometric titration with NaOH	7.5 (at first inflection)	6.5
		9.5 (at second inflection)	13.0
	Leaching with N $BaCl_2$ and estimation of adsorbed Ba	3.0 9.0	3.8 13.0

or the "cation effect" which operates in a method is particularly strong, will an agreement with the total charge indicated by the final inflection in the titration curve be found. The results in table 1 of base-exchange studies on hydrogen forms of mica, illite, and kaolinite fully bear out the foregoing conclusions.

The base-exchange capacity of the hydrogen mica calculated at the second inflection of its titration curve is 13.0 me. per 100 gm., which represents the contribution to the total base-exchange capacity of the isomorphous charge. Parker's method (10) indicates only this part of the total. Leaching with N BaCl_2 solution gives even smaller values when the pH values of the contact solutions are 1.5 and 6.0. The isomorphous charge is, therefore, not permanent in the sense that it is not independent of the pH, as Schofield (11) thought it would be. The reason is that the free H ions of the contact solution enter into an exchange competition with the metal cations—in this case, Ba ions—particularly when the pH of the solution is definitely on the acid side. It is only reasonable to expect that all the cations present in the leaching solution will compete for the negative charge of the surface, and the extent to which each will succeed will depend on valency and concentration. Evidently, for a fixed ratio of the concentration of H ions and that of a metal cation in the leaching solution, there will also be a fixed ratio of the quantities of these ions on the surface even after exhaustive treatment with the salt. At a given pH, if not very low, the ratio can be made vanishingly small; in other words, saturation of the surface by the metal cation can be made virtually complete if the valency of the cation is large and its concentration is high. It is only then that the "cation effect" overrides the "pH effect." It would be wrong to assume that the pH will have no effect regardless of the concentration and valency of the metal cation. An instance of complete masking of the pH effect by the cation effect, so far as the isomorphous charge is concerned, is seen when the hydrogen mica is leached with 8.5 N $\text{Ba}(\text{SCN})_2$ solution at pH 7.2. Under these conditions, the base-exchange capacity is definitely higher than the value which corresponds to the isomorphous charge. In fact, the cation effect is so strong that some of the hydroxylic hydrogens are also exchanged for the Ba ions. Leaching with this solution at pH 8.1 gives an exchange value equal to that obtained from the third inflexion of the titration curve though this inflection occurs at a much higher pH. The saturated solution (8.5 N) of $\text{Ba}(\text{SCN})_2$, therefore, gives a measure of the total charge, isomorphous and hydroxylic, at the comparatively low pH of 8.1. When N BaCl_2 is the leaching solution and the cation effect is, therefore, much weaker, a much higher pH is required.

Hydrogen illite, like hydrogen mica, has been found to give three inflections in its potentiometric titration curves with bases and, to make the analogy complete, the base-exchange capacities calculated at the third and second inflections in the titration curves of hydrogen illite are also as 3:1. On the basis of the structural similarity of hydrogen mica and hydrogen illite and the observed similarity of their titration curves, it is reasonable to assume that the second inflection in the titration curve of hydrogen illite indicates the contribution to its total base-exchange capacity of the "isomorphous charge," and the third inflection, the total charge made up of this isomorphous charge and the charge due to the available hydroxyl groups of the illite crystals. Parker's method and leaching with N $\text{Ba}(\text{SCN})_2$ give a higher value of the base-exchange capacity than does the titration curve at its second inflection point, though the pH in each case is lower than that at the second inflection. The strong adsorbability of the Ba ions

present at the high concentration of 1.0 *N* enables these ions to replace some of the hydroxylic hydrogens in addition to the H ions balancing the isomorphous charge. At the much higher concentration, 8.5 *N*, of the saturated $\text{Ba}(\text{SCN})_2$ solution, and at the higher pH of 8.5, the combined pH and cation effect is sufficiently strong to bring about a complete replacement of all available hydrogen ions on the surface, "isomorphous" as well as hydroxylic.

At the lower pH of the leaching solution, kaolinite absorbs a smaller quantity of Ba than that corresponding to the base-exchange capacity at the first inflection; the pH effect is much too weak for the strong cation effect to bring about a complete replacement of H ions derived from the more dissociable of the two categories of OH-groups. The observed agreement between the maximum up-

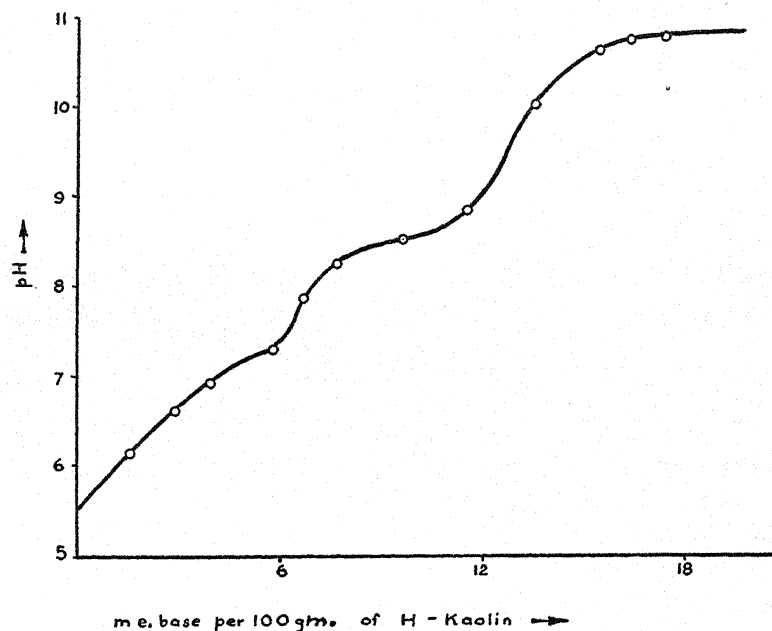


FIG. 2. TITRATION CURVE OF HYDROGEN KAOLINITE

take of Ba ions and the base-exchange capacity calculated at the second inflection lends support to the view that the second inflection stands for the upper limiting value of the exchange capacity of kaolinite. The first inflection (fig. 2) occurs at about pH 7.5, and on the assumption that it stands for the neutralization of the more dissociable OH-groups of the kaolinite lattice, these OH-groups apparently react with a base at a much lower pH than the OH-groups in mica and illite. The weaker acid character of the OH-groups in these three-layer minerals is to be attributed to the presence of H^+ , which balances the isomorphous charge. The dissociation and neutralization of these H ions in the first stage of the reaction with the base imparts a negative charge to the surface, and the electrostatic effect which is set up hampers the dissociation and neutralization of the OH-groups of the lattice.

ALLEGED CATION-BINDING POWER OF "BROKEN BONDS" DEVELOPED ON LATERAL SURFACES OF LAYER-LATTICE SILICATES

An idea has been gaining ground for some time among soil chemists and clay crystallographers that cations can be held on the lateral surfaces of clay crystals where unsatisfied negative charges or valences are developed as a result of lattice termination (2, 3). Indeed, this has been considered the explanation of the cation-binding power of clay minerals of the kaolin group that do not contain multi-coordinated metal cations in the lattice (required for balancing negative charges arising from isomorphous replacements) which can be exchanged for the cations of a contact solution. It has been suggested that the cations are taken up on the lateral surfaces of the sheets by unsatisfied negative valencies. The lateral surface increases on grinding. This produces fractures parallel to the C axis by breaking bonds between Si and O and between Al and O (or OH). The fact that the cation-binding power of kaolinite increases on grinding is, on this theory, to be attributed to an increase in the number of the "broken bonds." This explanation has been critically examined by Mukherjee *et al.* (9), who have pointed out that if a cation-binding power is to be attributed to the broken bonds, an anion-binding capacity due to the same cause must be simultaneously recognized, that is, the mineral must be considered amphoteric and not merely acidic. This follows directly from the principle of microscopic neutrality, which requires that potentially positive and negative ends or poles be produced simultaneously and in equivalent numbers by the rupture of the bonds. In a previous publication (8) arguments were advanced in support of the view that with clay crystals, as with most insoluble ionic crystals made up of closely packed oppositely charged ions, the odds will be very much against the spacings between the positive and negative poles created by comminution being large enough to admit of the creation of sufficiently strong negative and positive electrical fields external to the crystal to attract cations and anions from a contact solution and fix them to the solid wall. One would rather expect a mutual cancellation of the positive and negative fields of contiguous opposite poles, resulting in an inhibition or even complete suppression of a possible amphoteric character of the comminuted solid.²

Experiments with ground muscovite appear to confirm the aforementioned views. To 0.35-gm. samples of the mica, KCl and K_2SO_4 were added at concentrations ranging from 0.0015 *N* to 0.180 *N*, and after the mixtures stood overnight, the concentrations of Cl^- and SO_4^{--} in the contact solutions were determined. In no case could any difference be observed between the initial and final concentrations of either ion. The anions are, therefore, not taken up by the solid. This shows that the crystallites do not contain any free positive poles. And since there are no positive poles, there cannot be any free negative poles, for if the

² It is to be noted that the "broken bond theory" makes the tacit assumption that the bonds are predominantly ionic, and the criticism advanced here is directed against the one-sided view it takes, granting that the bonds are all ionic. This is doubtful, however, especially for the Si—O—Si bonds. They are perhaps mainly covalent in nature, in which case their broken ends may adsorb neutral atoms and molecules as water dipoles.

latter alone had existed, they would have drawn cations from a contact solution, and when the crystals were sieved out a solution containing more anions than cations would be left. This is manifestly impossible.

No amount of grinding of the crystals and no conceivable rearrangement of their building units that might follow the act of grinding could, therefore, give a net negative charge to the solid which would preferentially attract only cations from the solution and fix them to the solid wall. If cations must be taken up from the contact solution, an equivalent quantity of one or another cationic constituent of the solid crystal lattice will have to be supplied. In other words, the only type of electrochemical or ionic reaction in which the crystals can take part, aside from decomposition and other secondary changes, is one of cation exchange, as the more common anions are not taken up by the crystals. The cationic constituents that are bonded to the crystal by the weakest link will be exchanged. Clearly, they will be the large monovalent or bivalent metal cations of the lattice which also have the largest coordination number, such as the K ions in muscovite. Such of these metal cations as can come in contact with a solution will be exchanged for the cations of the solution, for example, the H ions of an acid, and these H ions can again be exchanged for the cations of a salt or a base.

Using hydrogen mica, in which the significance of each stage of this exchange reaction can be readily appreciated, the authors have been able to locate the "end point" in the form of an inflection in the titration curve with a base. The electrochemical reactivity of the system, however, does not end here. It takes part in another cation-exchange reaction in which the H ions of the accessible OH-groups of the crystal are involved. In view of the strong bond between the oxygen and the hydrogen of the hydroxyl group, however, rather drastic conditions must be created to enable the hydroxylic hydrogens to take part in an exchange reaction. The necessary condition is ensured if either the OH-ion concentration of the contact solution is high or the concentration as well as the valency of the exchanging metal cation is sufficiently large—in other words, if either the "pH effect" or the "cation effect" is particularly strong. Hydrogen ions of accessible OH-groups are exchanged under these conditions. There is a definite end point of this exchange reaction also. It is seen either as the final inflection in the titration curve with a base or as the limiting high value of the quantity of cations that a given weight of the mineral takes up from a contact solution. The base-exchange and titrimetric work on hydrogen mica, in particular, shows that the limiting value of the base-exchange capacity is completely accounted for by the isomorphous and hydroxylic charges, and no recourse need be had to any broken bond hypothesis to explain any part of the limiting base-exchange capacity.

SUMMARY

The negative (surface) charge of a clay crystal, which is responsible for its base-exchange or base-combining capacity, has a definite limiting value and is caused partly by isomorphous replacements of cations within the lattice and partly by dissociation of the available OH-groups of the crystal. Quantitative

agreement between the theoretical ratio of these two types of charges and its experimentally determined value has been observed for hydrogen mica. The total negative charge, "isomorphous" and "hydroxylic," is revealed by the final inflection in the titration curve of the hydrogen mineral with a base, provided secondary effects, such as decomposition of the clay, do not occur. Analytical methods of determining the base-exchange capacity which depend on estimating the amount of cations taken up by a clay from solutions of salts, as a rule, give results which are too low compared with the total charge, and only in rather exceptional cases, when either the pH is sufficiently high or the valency and concentration of the cations in the contact solution are large, is an agreement found between the analytically determined base-exchange capacity and that calculated from the final inflection in the titration curve.

REFERENCES

- (1) HAUSER, E. A., LE BEAU, D. S., AND PEVEAR, P. P. 1951 Surface structure and composition of colloidal siliceous matter. *Jour. Phys. and Colloid. Chem.* 55: 68-79.
- (2) HENDRICKS, S. B. 1945 Base exchange of crystalline silicates. *Indus. and Engin. Chem.* 37: 625-630.
- (3) KELLEY, W. P., AND JENNY, H. 1936 Relation of crystal structure to base exchange and its bearing on base exchange in soils. *Soil Sci.* 41: 367-382.
- (4) MARSHALL, C. E. 1935 Layer lattices and the base exchange clays. *Ztschr. Krist.* 91(A): 433.
- (5) MITRA, R. P., AND MITRA, A. K. 1940 Base binding capacities of hydrogen clays as determined by different methods. *Indian Jour. Agr. Sci.* 10: 344-351.
- (6) MITRA, R. P. 1942 Electrochemical aspects of ion exchange in clays, bentonites and clay minerals. *Indian Soc. Soil Sci. Bul.* 4: 41-147.
- (7) MITRA, R. P., AND RAJAGOPALAN, K. S. 1948 Electrical charges in layer-lattice silicates in relation to ionic exchange. *Indian Jour. Phys.* 22: 129-140.
- (8) MITRA, R. P., AND RAJAGOPALAN, K. S. 1948 Titration curves of hydrogen mica. *Nature* 162: 104-105.
- (9) MUKHERJEE, J. N., et al. 1942 Nature of reactions responsible for soil acidity: VIII. *Indian Jour. Agr. Sci.* 12: 86-101.
- (10) PARKER, F. W. 1929 Determination of exchangeable hydrogen in soils. *Jour. Amer. Soc. Agron.* 21: 1030-1039.
- (11) SCHOFIELD, R. K. 1939 Electrical charges on clay particles. *Soils and Fert.* 2: 1-5.
- (12) WRIGHT, C. H. 1934 *Soil Analysis—a Handbook of Physical and Chemical Methods.* Thomas Murby, London.

EFFECT OF IRON AND ALUMINUM OXIDES ON THE RELEASE OF CALCIUM AND ON THE CATION-ANION EXCHANGE PROPERTIES OF SOILS

A. MEHLICH

North Carolina Agricultural Experiment Station¹

Received for publication September 8, 1951

It is now reasonably well established that the type of colloid has a significant influence on the "activity" (12) and chemical release (1, 16) of Ca. Likewise, the Ca content of plants has been shown to be influenced by colloid type (1, 4, 15). Most of the studies reported have emphasized effects of members of the 1:1 and 2:1 mineral lattice families. Very little consideration has been given to the possible influence of hydrated iron and aluminum oxides on the release of Ca. In view of the association of large amounts of such oxides as gibbsite, goethite, and hematite with clay minerals, notably those of the 1:1 lattice family (6), an investigation was undertaken to study the influence of the oxides on the release of cations. Soils known to vary greatly in these constituents were used to measure the release of Ca with HCl. Hematite, goethite, precipitated iron and aluminum hydroxides, and Amberlite IR-4B were added to soils representing the 1:1 and 2:1 lattice families. The effect on the release of Ca with HCl and on the growth and cation content of cotton and turnips was determined. Measurements were made of the cation- and anion-exchange capacities of the various systems.

EXPERIMENTAL PROCEDURES AND RESULTS

Release of Ca as affected by type of colloid and degree of Ca saturation

The soils used were Cecil B horizon from Rutherford County, North Carolina; Cecil B horizon from Wake County, North Carolina; Georgeville B horizon and White Store B horizon, both from Chatham County, North Carolina; Fannin C horizon from Macon County, North Carolina; and Nipe A horizon from Puerto Rico.

Iron and Al oxides were removed by digesting 50-gm. portions of soil in 450 ml. of H₂O and 50 ml. concentrated HCl for about 2 hours. After this treatment, the North Carolina soils were whitish-gray, and the Nipe was dark brown. The treatment was repeated with the soils high in oxides, Fannin and Nipe. They were then filtered, washed with copious quantities of H₂O and dried at 45°C. Colloid separates less than 2 μ were made, and the mineral composition was approximated by x-ray analysis. The results of these analyses are shown in table 1. The HCl treatment was effective in reducing gibbsite, hematite, and

¹ Contribution from the department of agronomy, North Carolina Agricultural Experiment Station, Raleigh. Published with the approval of the director as Paper 398 of the journal series. The author is indebted to M. L. Jackson, University of Wisconsin, for the x-ray analysis and to N. T. Coleman, North Carolina Agricultural Experiment Station, for the differential thermal analysis.

goethite in all soils except Nipe. As a consequence of this treatment, the colloids were richer in kaolinite. The White Store colloid was characterized by means of different thermal analysis. The untreated sample was found to consist of approximately 70 per cent montmorillonite and 20 per cent kaolinite. The proportions were about the same after HCl treatment.

TABLE 1
Approximate mineral content of untreated and treated soil colloids*

SOILS OR MINERALS	MINERAL COMPOSITION							
	Kaolinite		Gibbsite		Hematite		Goethite	
	Un-treated	Treated	Un-treated	Treated	Un-treated	Treated	Un-treated	Treated
	%	%	%	%	%	%	%	%
Cecil B (Rutherford Co.).....	45	80	30	10	15	0	0	0
Cecil B (Wake Co.).....	70	90	tr.	tr.	15	0	10	0
Georgeville B (Chatham Co.).....	70	90	0	0	15	0	0	0
Fannin C (Macon Co.).....	25	90	40	tr.	15	0	15	0
Nipe (Puerto Rico).....	15	40	15	25	20	0	50	30

* Digested with HCl.

TABLE 2
Equilibrium pH and cation- and anion-exchange capacities of soils untreated and treated to remove Fe and Al oxides

SOIL	pHe		CATION-EXCHANGE CAPACITY		ANION-EXCHANGE CAPACITY		CATION-ANION RATIO	
	Untreated	Treated	Untreated	Treated*	Untreated	Treated*	Untreated	Treated
			me.	me.	me.	me.		
Cecil (R).....	5.2	3.3	6.4	10.0	15.9	10.4	0.4	1.0
Cecil (W).....	3.9	3.1	10.2	14.0	14.9	12.0	0.7	1.2
Georgeville.....	4.0	3.0	8.2	12.5	12.5	6.8	0.7	1.8
Fannin.....	5.2	3.7	4.0	5.2	10.6	4.5	0.4	1.2
Nipe.....	5.3	4.7	12.8	17.8	28.0	32.0	0.4	0.6
White Store.....	2.9	2.7	32.4	28.4	12.2	9.0	2.6	3.2

* The cation- and anion-exchange capacities of these samples are based on the weight of the soil after treatment. To obtain these properties based on the original weight, multiply in the above order by: 0.68, 0.82, 0.80, 0.66, 0.45, and 0.95.

The cation- and anion-exchange properties of the soils were determined by a method² previously described (18). The results shown in table 2 indicate that the HCl-treated soils, except White Store and Nipe, have higher cation-ex-

² Cation-anion ratios previously were calculated on the basis of milliequivalents cation-exchange capacity/millimoles anion-exchange capacity. Expressing the latter also as milliequivalents gives results more descriptive of the relationships involved. This method is used hereafter.

change and lower anion-exchange capacities. The cation-anion ratios of the treated soils are invariably greater than those untreated.

Additions of $\text{Ca}(\text{OH})_2$ were made to give two levels of Ca, approximately 40 and 80 per cent saturation (table 3). Following daily shaking for 1 week, the suspensions were filtered, the soils dried at 45°C ., and the Ca in the filtrate was determined. The percentage Ca saturation in soil listed in table 3 was calculated from the difference of the $\text{Ca}(\text{OH})_2$ added and the Ca found in solution. Amounts of soil weighed to supply 0.2 me. Ca were treated with an equivalent amount of HCl in a total volume of 100 ml. The samples were shaken for 15 minutes, filtered, and the Ca was determined.

TABLE 3
Release of Ca by addition of equivalent concentrations of HCl

SOIL	pH		Ca SATURATION		Ca RELEASED*	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
			%	%	%	%
Cecil (R)						
low Ca.....	4.7	5.2	33	31	67	33
high Ca.....	6.8	7.2	66	58	64	59
Cecil (W)						
low Ca.....	4.6	4.6	43	41	53	38
high Ca.....	6.8	7.6	81	83	56	55
Georgeville						
low Ca.....	4.8	5.2	43	45	55	38
high Ca.....	6.8	7.9	84	86	60	54
Fannin						
low Ca.....	5.3	5.6	38	35	66	54
high Ca.....	7.3	8.3	80	87	68	63
Nipe						
low Ca.....	5.8	5.8	34	34	76	57
high Ca.....	7.0	7.6	69	90	82	73
White Store						
low Ca.....	4.9	4.6	50	44	42	27
high Ca.....	7.4	7.2	95	87	52	38

* Percentage of exchangeable Ca.

The percentages of Ca released are presented in table 3. The HCl-digested soils released less Ca than the natural soils, notably at the lower levels of Ca. This difference is less pronounced with Fannin and Nipe.

*Release of Ca as affected by additions of iron and aluminum oxides to
Georgeville soil*

The materials used were: hematite from Negaunee, Michigan; goethite from Ishpeming, Michigan; bauxite from Bauxite, Arkansas³; Commercial c.p.

³ These materials were obtained from Wards Natural Science Establishment, Rochester, New York.

$\text{Al}(\text{OH})_3$, freshly precipitated ferric oxide hydrate, and freshly precipitated aluminum oxide hydrate.

The oxide hydrates of Fe and Al were prepared from their chlorides with NH_4OH . The bulk of the excess salts was removed by repeated additions of H_2O and siphoning through Mandler filtering candles. Although this process was carried on for about 3 weeks, Cl ions in the Al oxide hydrate were still detectable.

The hematite and goethite were ground, and the fraction passing a 200-mesh sieve was used. The massive bauxite (listed as $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) contained grayish red, red, and dark red crystals. Differential thermal analysis showed the grayish red fraction richer in gibbsite than the others and it was used. These materials and the precipitated oxides were added to 4-gm. portions of the HCl-digested Georgeville soil in amounts to provide 20 per cent of the oxide materials. Calcium hydroxide was added to give approximately 25, 50, 75, and 100 per cent Ca

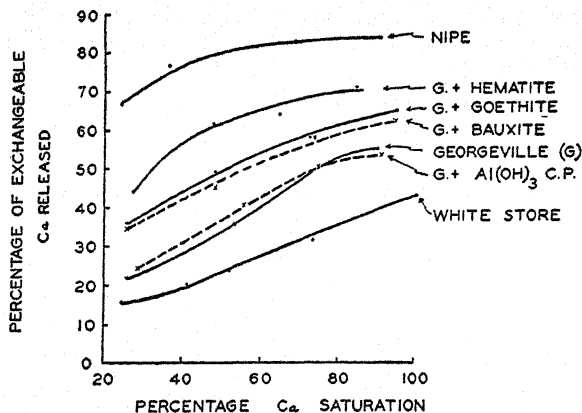


FIG. 1. PERCENTAGE RELEASE OF Ca FROM NIPE, WHITE STORE (HCl-DIGESTED), GEORGEVILLE (HCl-DIGESTED), AND GEORGEVILLE PLUS SESQUIOXIDE MIXTURES. HCl ADDED IN AMOUNTS EQUIVALENT TO THE EXCHANGEABLE Ca.

saturation. The systems were made to 100 ml. with H_2O and shaken daily for 8 days. The pH was measured, the suspensions were filtered, and the soils dried at 45°C . Calcium in the filtrate was determined, and Ca on the soil was calculated by difference. HCl was then added in amounts equivalent to the Ca on the soil. The systems were again diluted to 100 ml. with H_2O , shaken for 15 minutes, filtered, and the Ca in solution was determined. The residual mixtures were then used to determine the cation- and anion-exchange capacities and pHe.

The results showed the oxide additions to have little influence on cation-exchange capacity. The anion-exchange capacity and pHe were increased markedly only by addition of the $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$.⁴

The results pertaining to the Ca release are shown in figure 1. The majority of the oxide treatments induced an increase of Ca in solution. The addition of

⁴ Data not shown.

$\text{Al}(\text{OH})_3$ (c.p.), $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$, and $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ had no effect on the release of Ca.⁵ Data on the release of Ca from a soil high in montmorillonite (White Store) and from a soil high in iron oxides (Nipe) have been included in figure 1 for comparison. The results show Ca release lowest from the montmorillonitic soil and highest from the high iron oxide soil.

Growth and cation content of cotton and turnip tops as affected by additions of Amberlite and iron and aluminum oxides to White Store soil

The work with White Store soil involved the release of Ca with HCl and greenhouse studies on the uptake of Ca by cotton and turnip tops. The White Store soil was a bulk collection from the location described. Its cation-exchange capacity was only 25 me. as compared to 32.4 for the sample reported in table 2. The exchangeable cation content in milliequivalents per 100 gm. was: H-23, Ca-0.63, Mg-1.48, and K-0.42. Thousand-gram portions of the soil were weighed into 2-gallon glazed pots, and sufficient $\text{Ca}(\text{OH})_2$, MgCO_3 , and K_2HPO_4 were added to give a total of 100, 50, and 10 me. per pot of Ca, Mg, and K, respectively. Sufficient H_2O was added to make a soft paste. This was mixed several times daily. After 5 days, to different pots were added 40 gm. hematite, 13 gm. iron oxide hydrate, 100 gm. Amberlite IR-4B,⁶ and 2,500 gm. Fannin soil. The last two materials were added in these amounts to give approximately 250 me. anion-exchange capacity. The anion-exchange capacity of Amberlite IR-4B was 250 and that of the Fannin soil was 10.6, obtained by a method described previously (18). The Fannin soil was used because of its high gibbsite content (see table 1).

The soft paste of the mixtures was again stirred daily for 8 days. Then, amounts of quartz sand were added to give a total weight of 5,000 gm. After thorough mixing, the materials were spread out on paper until air-dry. They were then ground to pass a 2-mm. sieve and four 1,000-gm. portions were weighed into percolator cylinders.

A parallel experiment involved mixtures of White Store and Nipe. Nipe was selected because of its high iron oxide content. The White Store and Nipe soils were treated with $\text{Ca}(\text{OH})_2$, MgCO_3 , and K_2HPO_4 as previously described. These soils were then mixed in various proportions (see table 5), and 1,000-gm. portions were weighed into percolator cylinders.

On May 12, 1950, five seeds of cotton per cylinder were placed slightly below the surface, and the cylinders were covered with filter paper to reduce evaporation. Sufficient H_2O was added daily to maintain optimum moisture. After germination, the stand was reduced to one plant per cylinder. On May 18 and June 1, 20 mgm. N as NH_4NO_3 was added to each cylinder. The aerial parts were harvested on June 16. The second crop, turnip (var. Seven Top), was seeded on January 6, 1951 and harvested on February 26. Dry weights and the Ca, Mg, and K contents of cotton and turnip tops were measured.

⁵ Data for last two treatments not shown.

⁶ Obtained through the courtesy of the Rohm and Haas Company, Resinous Products Division, Philadelphia.

Soil samples taken before the seeding of cotton and after the harvesting of turnips were analyzed for reaction and for cation- and anion-exchange properties. The results dealing with the mixtures of White Store and iron oxide and of White Store and Amberlite are shown in table 4, and those of the White Store-Nipe mixtures are shown in table 5.

Release of cations with HCl. The effects of iron-oxide-Amberlite additions to White Store on the Ca, Mg, and K released by HCl are shown in table 6. HCl added in amounts equivalent to the sum of the metal cations present (table 4)

TABLE 4

Reaction and cation- and anion-exchange properties of mixtures of White Store and iron oxide and of White Store and Amberlite

MATERIALS	CATION EX- CHANGE	ANION EX- CHANGE	C/A	pHe	pH AND EXCHANGEABLE CATIONS							
					Before cotton				After turnips			
					pH	Ca	Mg	K	pH	Ca	Mg	K
	me.	me.				me.	me.	me.		me.	me.	me.
Soil only.....	5.1	3.0	1.7	3.1	5.3	1.9	1.0	.19	5.2	1.4	.89	.09
Soil + hematite.....	4.8	3.1	1.5	3.0	5.0	2.2	1.1	.20	5.0	1.4	.91	.09
Soil + 1.3 per cent $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$	4.7	3.0	1.6	3.0	5.5	2.3	1.1	.19	5.2	1.2	.80	.07
Soil + Amberlite IR-4B.....	4.7	9.0	0.5	4.0	6.4	2.1	1.0	.21	5.3	1.2	.74	.06
Soil + Fannin.....	6.2	9.4	0.7	3.9	5.6	1.9	1.1	.20	4.9	1.6	.93	.15

TABLE 5

Reaction and cation- and anion-exchange properties of mixtures of White Store and Nipe

WHITE STORE	NIPE	CATION- EXCHANGE CAPACITY	ANION- EXCHANGE CAPACITY	CATION- ANION RATIO	pHe	pH AND EXCHANGEABLE CATIONS							
						Before cotton				After turnips			
						pH	Ca	Mg	K	pH	Ca	Mg	K
per cent	per cent	me.	me.				me.	me.	me.		me.	me.	me.
100	0	5.1	3.0	1.7	3.0	5.3	1.9	1.0	.19	5.2	1.4	.89	.09
75	25	4.8	5.8	0.8	3.5	6.4	2.2	1.0	.20	5.3	1.2	.81	.07
50	50	4.9	7.1	0.7	4.1	6.5	2.3	0.8	.20	5.9	1.2	.68	.07
25	75	5.1	8.0	0.6	4.5	6.7	1.9	0.8	.21	6.2	1.1	.65	.06
0	100	4.9	9.7	0.5	5.3	6.7	2.0	0.8	.22	6.5	1.1	.56	.06

released somewhat more Ca and Mg from the soils mixed with the iron oxides. In the presence of Amberlite, Ca and Mg in solution was lower than in the untreated soil. The data for the White Store-Nipe mixtures (table 7) show increasing amounts of Ca and Mg in solution with increasing proportions of Nipe to White Store.

Cation content of cotton and turnip tops. The results of the analysis for Ca, Mg, and K in cotton and turnip tops are shown in tables 8 and 9. Table 8 records the data on the mixtures of White Store and iron oxide and of White Store and Amberlite. As a result of adding the iron oxides, the Ca content was significantly increased in cotton and turnips. Hematite effected an increase of

Ca in cotton but not in turnips. The addition of Amberlite resulted in a decrease of Ca in cotton and an increase in turnip tops. The Ca was likewise low

TABLE 6

Release of cations with HCl added in amounts equivalent to the exchangeable bases from mixtures of White Store and iron oxide and of White Store and Amberlite

MATERIALS	CATIONS RELEASED			
	Ca	Mg	K	Total released
	me.	me.	me.	per cent
Soil only.....	0.82	.54	.10	47
Soil + hematite.....	1.05	.68	.10	52
Soil + 1.3 per cent $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$	0.98	.63	.10	48
Soil + Amberlite IR-4B.....	0.70	.48	.12	39
Soil + Fannin.....	0.82	.60	.10	48

TABLE 7

Release of cations with HCl from mixtures of White Store and Nipe

WHITE STORE	NIPE	CATIONS RELEASED			
		Ca	Mg	K	Total Release
		me.	me.	me.	per cent
100	0	0.82	.54	.10	47
75	25	1.15	.65	.10	56
50	50	1.26	.68	.10	62
25	75	1.40	.64	.12	71
0	100	1.60	.73	.16	83

TABLE 8

Dry weights and cation contents of cotton and turnip tops grown on mixtures of White Store and iron oxide and of White Store and Amberlite

MATERIALS	COTTON					TURNIP TOPS				
	Dry weight	Ca	Mg	K	Sum	Dry weight	Ca	Mg	K	Sum
	gm.	me.	me.	me.	me.	gm.	me.	me.	me.	me.
Soil only.....	.52	118	99	43	260	0.95	59	31	63	153
Soil + hematite.....	.40	129*	100	45	274	0.84	62	35	99*	196
Soil + 1.3 per cent $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$52	142*	104	31†	277	1.14	82*	33	77*	192
Soil + Amberlite IR-4B....	.23†	71†	81†	37	189	1.01	75*	32	63	170
Soil + Fannin.....	.43	80†	90†	28†	198	Failure				

* Significantly higher than the untreated soil.

† Significantly lower than the untreated soil.

in cotton grown in the White Store-Fannin soil mixture. The results with the White Store-Nipe mixtures (table 9) show that the Ca contents of cotton and turnips increased with increasing proportions of Nipe up to the 50 per cent level.

The Ca subsequently decreased, and it was lowest in cotton grown on Nipe. The reason for this is not clear, although it may be pointed out that the plants grown on this treatment were significantly higher in K, thus probably resulting in a lower uptake of Ca through competitive ion effects.

TABLE 9
Dry weights and cation contents of cotton and turnip tops grown on mixtures of White Store and Nipe

WHITE STORE	NIPE	COTTON					TURNIP TOPS				
		Dry weight	Ca	Mg	K	Sum	Dry weight	Ca	Mg	K	Sum
<i>per cent</i>	<i>per cent</i>	<i>gm.</i>	<i>mc.</i>	<i>mc.</i>	<i>mc.</i>	<i>mc.</i>	<i>gm.</i>	<i>mc.</i>	<i>mc.</i>	<i>mc.</i>	<i>mc.</i>
100	0	.52	118	99	43	260	0.95	59	31	63	153
75	25	.48	120	97	43	260	1.10	71*	30	72*	173
50	50	.46	145*	101	42	288	0.90	114*	43*	70*	227
25	75	.52	142*	94	47	283	0.87	110*	50*	73*	233
0	100	.48	91†	86†	52*	229	0.99	109*	48*	88*	245

* Significantly higher than 100 per cent White Store soil.

† Significantly lower than 100 per cent White Store soil.

DISCUSSION

The results of this investigation again demonstrate a significant influence of type of colloid on the release of Ca. The data further show that this effect is not restricted to the well-defined clay minerals but that the hydrated iron and aluminum oxides play a role as well. There is evidence that the release of Ca increases inversely with the cation-anion-exchange capacity ratios. If, as previously assumed (5, 18), the cation-anion ratio and pH_e are a measure of the acidoid strength of soil colloids, it follows that more Ca is released with decreasing strength of the soil acidoid. The reaction, on addition of HCl to a Ca-soil, will thus proceed more nearly to completion, the weaker the acidoid.

The cation-anion ratios of colloids of the 1:1 and 2:1 lattice families range between 1 and 3. They are less than 1 whenever appreciable amounts of goethite, gibbsite, and hematite are present (19). The difference in these ratios as a function of the acidoid strength of colloids can be visualized on the basis of the differences in their mineralogical structure (7, 8) and of the dissociation of cations (11) from colloids of the 1:1 and 2:1 lattice families. The lower ratios for the colloids containing crystalline hydrated iron and aluminum oxides likewise are readily visualized. The explanation is offered that the hydrated oxides may affect the position and nature of the Ca-bond on the cation-exchange surface. The oxides may possess a negative charge sufficient to retain Ca but with a bonding sufficiently weak to afford a high release of Ca with HCl. The function of the former could be construed as a "blocking effect" whereby Ca would occupy, for the most part, easily accessible positions and not enter any part of the inner crystal structure. The entry of Ca into inner positions of the kaolinite structure has been suggested by Borland and Reitemeier (2). The

probability that Ca is held as exchangeable ions on the surface of hydrated oxides merits consideration in view of the observation by Prescott and Arthur (22) and the recent findings by Schuylenborgh (23) that naturally occurring oxides monohydrates, and hydroxides of iron and aluminum have lower isoelectric points than the amorphous laboratory preparations reported by Mattson (14). Schuylenborgh also found the isoelectric point of synthetically prepared hydrated iron oxides to be lower when heated to 60 to 100°C.

The exchange properties of the oxides used in the present study as well as the effect of heating on the release of Ca have been investigated. The results presented in table 10 show that the naturally occurring oxides have both cation- and anion-exchange capacities. Their cation-anion ratios are very low. Their percentage calcium releases are high, their fH values are low. The gibbsite was a laboratory preparation obtained by decomposing potassium aluminate with CO₂. The differential thermal analysis of this material showed some H₂O loss at 150°C. and a strong endothermic reaction at 320°C. This material, as shown

TABLE 10
Exchange properties of iron and aluminum oxides

OXIDE	CATION- EXCHANGE CAPACITY	ANION- EXCHANGE CAPACITY	CATION- ANION RATIO	pHe	Ca RELEASED	fH*
	<i>me.</i>	<i>me.</i>			<i>per cent</i>	
Hematite.....	2.7	4.5	0.6	5.5	94	0.1
Goethite.....	4.1	11.8	0.3	6.2	87	0.1
Bauxite.....	2.2	5.9	0.4	6.0	90	0.1
Gibbsite†.....	5.5	16.5	0.3	6.8	70	0.4

* After Bray (3), obtained from the ratio of residual percentage base saturation to percentage Ca released.

† Synthetic preparation obtained by decomposing potassium aluminate with CO₂.

in table 10, exhibits properties similar to those of the naturally occurring minerals, although Ca release is somewhat lower. Prolonged heating (at 105°C.) of the precipitated iron and aluminum oxide hydrates did not effect greater release of Ca.

To account for the greater Ca release in mixtures containing sesquioxides, the possibility of the entrance of Fe or Al ions (brought into solution by HCl) into an exchange reaction with Ca was also considered. Since it is well known that trivalent ions are more effectively adsorbed by colloids than are either divalent or monovalent ions (13, 21), it may be supposed that these ions would induce greater release of Ca. HCl, FeCl₃, and AlCl₃ were added in different ratios to an 80 per cent Ca-saturated Georgeville soil, and the Ca and H in solution were measured. The results (fig. 2) show FeCl₃ to be equally effective and AlCl₃ to be more effective than HCl. From this it may be concluded that the Al entered into an ionic-exchange reaction, whereas the Fe did not. This observation is in agreement with many previous findings that Al is present more preponderantly as an exchangeable ion than is Fe (20, 21). The release

of Ca with FeCl_3 was probably induced by the product of its hydrolysis, namely, HCl .

In view of the greater effectiveness of Al than H in replacing Ca, it follows that the release of Ca from a Ca-Al-H-clay should be greater than that from a Ca-H-clay. On the basis of the complementary ion principle, the substitution of an ion having a lower oscillation volume (9) or "ease of release" (3) value for one having a higher value should increase the release of the complementary ion. The lower fH values obtained in the Al systems (fig. 2) may be taken as evidence of this effect.

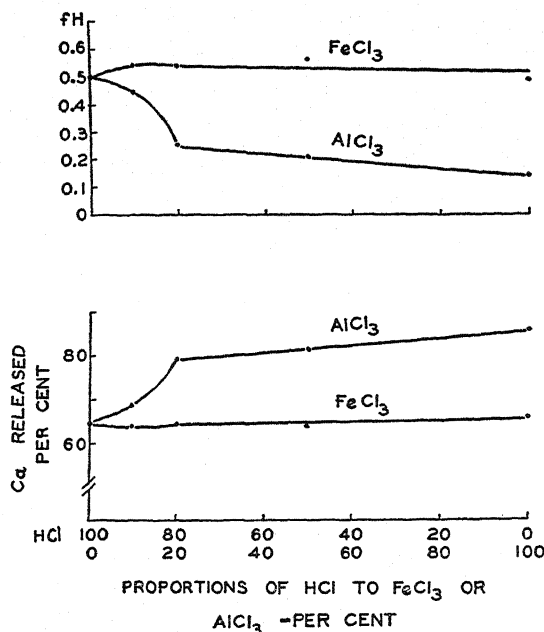
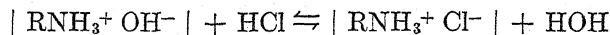


FIG. 2. PERCENTAGE Ca RELEASED AND fH VALUES WITH HCl , FeCl_3 AND AlCl_3 ADDITIONS TO GEORGEVILLE SOIL (80 PER CENT Ca SATURATED). THE AMOUNTS ADDED WERE EQUIVALENT TO EXCHANGEABLE Ca ON THE SOIL.

Analysis of the cotton and turnip tops showed that iron oxides increased the mobilization of Ca into the plants and increased Ca released by HCl . The influence of Amberlite, in one case reducing the uptake of Ca, and in another promoting it, requires further elucidation.

According to Kunin and Myers (10, p. 41) the neutralization reaction of an anion exchanger proceeds as follows:



The reduced adsorption of metal cations by cotton grown on the mixtures of White Store and Amberlite may have resulted from the partial neutralization of root-derived H ions by OH groups on the anion-exchange surface. This would leave fewer H ions available for exchange with the metal cations on the

cation-exchange surface. The following crop, turnips, was no longer influenced by this property, probably because by this time the OH groups were replaced largely by the bicarbonate and nitrate anions. The end product of the root-derived H ions would then yield HNO_3 , or H_2CO_3 in place of HOH. To check on this, 0.5 symmetry HCl was added to the White Store-Amberlite mixtures at the conclusion of the experiment. The result showed the sum of the metal cations and H in solution to be 78 per cent as compared to 51 per cent for the soil before cotton. Neutralization of excess acid was still indicated, but the effect was less pronounced.

This problem was further investigated by varying the concentrations of HCl and measuring the release of the metal cations as well as the H remaining in solution by titrating with NH_4OH to pH 6.5. The results with the mixtures of White Store and Amberlite, iron oxide, and Fannin (soil high in gibbsite) are shown in table 11. At the lowest levels of HCl added, release of Ca and H remaining in solution was less in the Amberlite or Fannin systems than in the

TABLE 11

Bases and H in solution after addition of increasing amounts of HCl to the mixtures of White Store and Amberlite or oxide

MATERIALS	HCl ADDED—me./100 gm.					
	1.0		2.5		5.0	
	Bases	H	Bases	H	Bases	H
	me.	me.	me.	me.	me.	me.
Soil only.....	0.75	0.13	1.28	1.35	1.45	3.65
Soil + $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$	0.82	0.10	1.70	0.90	1.76	3.32
Soil + Amberlite IR-4B.....	0.50	0.03	1.20	0.19	1.62	1.74
Soil + Fannin.....	0.63	0.03	1.38	0.50	1.75	2.47

untreated soil. At the highest level of HCl, release of metal cations was greater from the mixtures than from the soil only. The results clearly show that with the untreated soil and the mixture of soil and $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$, the sums of metal cations released and the H remaining in solution were equal to the initial concentrations of HCl added. With the mixtures of soil and Amberlite or Fannin, the discrepancy (failure to account for all of the H) increased with decreasing amounts of HCl supplied.

A similar study was made with mixtures of Georgeville soil and sesquioxides. The results showed that nearly complete accounting of the Ca released and H in solution could be made whenever well-crystallized oxides, such as goethite, were used. When the amorphous $\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ was used, only 53 and 65 per cent of the cations involved in the reaction could be accounted for when the additions of HCl were 0.25 and 1 symmetry concentrations, respectively.

The neutralization of HCl by the synthetic anion exchanger appears to be well understood. The nature of its neutralization by the aluminum oxide hydrates is not clear, unless it is assumed that compounds such as $\text{Al}(\text{OH})_2\text{Cl}$ or $\text{AlO}(\text{HCl})_2$ are formed. This has not been verified, although the presence of active OH

groups has been indicated in that the addition of KCl to freshly precipitated aluminum oxide hydrate increased the pH from 6.4 to 7.1. Such an effect was not observed with the natural iron or aluminum oxides. Furthermore, neutralization of HCl added to the aluminum oxide hydrate in an aqueous and in a *N* KCl suspension was 8 and 31 per cent, respectively. The same effect was given by CaCl_2 . Whenever the soil contains amorphous aluminum oxide hydrates, a portion of the H added is apparently tied up with such compounds, thus rendering replacement of the exchangeable metal cations less complete. If not already present in certain "young soils," amorphous aluminum oxide hydrates may also be formed when acid soils containing exchangeable Al are limed with $\text{Ca}(\text{OH})_2$. It may be suggested that under these conditions the so-called "overliming injury" may be due to the inability of the plant to obtain the needed exchangeable cations, since a portion of the root-derived H^+ would be neutralized by the active OH groups. It also follows that this "injury" would be greater, the lower the metabolic activity of the plant species involved.

The more prominent effect of hydrated iron or aluminum oxides, however, is an increased mobility of metal cations through exchange with H ions. This effect is due in part to the retention of metal cations above the pH of the isoelectric point in easily replaceable form and in part to a buffering effect by anion-exchange surfaces. Release of metal cations by H will proceed to greater completion, since the end product formed is in the nature of a very weak acid. The determination of fH and cation-exchange-anion-exchange-capacity ratios should serve as useful criteria for ascertaining the relative availability of cations. Both criteria would help to predict the percentage Ca saturation necessary for optimum plant growth, as was suggested previously (16, 17).

SUMMARY

The effect of type of colloid, including montmorillonite, kaolinite, gibbsite, goethite, and hematite, on the release of Ca with HCl and on the content of cations of cotton and turnip tops has been studied. In some of these experiments the anion exchanger IR-4B in a mixture with a montmorillonitic soil was studied. The cation-and anion-exchange capacities of the various systems were determined. The principal results obtained were:

Release of Ca increased with increasing degree of saturation and, at a given percentage Ca level, increased in the order: montmorillonite, kaolinite, kaolinite-gibbsite-bauxite-hematite-goethite mixtures. Release of Ca and the Ca content of cotton and turnip tops were increased with additions of hematite, iron oxide hydrate, and a soil (Nipe) high in goethite and hematite. In presence of the anion exchanger IR-4B, Ca was decreased in cotton and increased in turnip tops (second crop grown). Release of Ca in this system was decreased with small additions of HCl but increased with large additions (1 symmetry). The results were similar with aluminum oxide hydrate.

In general, release of Ca increased with decreasing cation-exchange-anion-exchange-capacity ratios, that is, decreasing strength of H-colloids.

With extremely low cation-anion ratios, however, in presence of very active

OH groups on an anion exchanger or on aluminum oxide hydrate, release or availability of Ca was suppressed. This was due to the partial neutralization of H by these groups, thus leaving less H available for replacement of Ca from the cation-exchange surface.

Certain of the iron and aluminum oxide minerals were found to possess cation-exchange capacity. Release of Ca from these minerals was very high.

Release of Ca was greater with the addition of AlCl_3 than with either FeCl_3 or HCl .

REFERENCES

- (1) ALLAWAY, W. H. 1945 Availability of replaceable calcium from different types of colloids as affected by degree of calcium saturation. *Soil Sci.* 59: 207-217.
- (2) BORLAND, J. W., AND REITEMEIER, R. F. 1949 Kinetic exchange studies on clays with radioactive calcium. *Soil Sci.* 69: 251-260.
- (3) BRAY, R. H. 1942 Ionic competition in base exchange reactions. *Jour. Amer. Chem. Soc.* 64: 954-963.
- (4) CHU, T. S., AND TURK, L. M. 1949 Growth and nutrition of plants as affected by degree of base saturation of different types of clay minerals. *Mich. Agr. Exp. Sta. Tech. Bul.* 214: 1-47.
- (5) COLEMAN, N. T., AND MEHLICH, A. 1949 Some chemical properties of soils as related to their cation exchange-anion exchange ratios. *Soil. Sci. Soc. Amer. Proc.* (1948) 13: 175-178.
- (6) COLEMAN, N. T., JACKSON, M. L., AND MEHLICH, A. 1950 Mineral composition of the clay fraction: II. *Soil Sci. Soc. Amer. Proc.* (1949) 14: 81-85.
- (7) GRIM, R. E. 1942 Modern concepts of clay minerals. *Jour. Geol.* 50: 225-275.
- (8) HENDRICKS, S. B. 1942 Lattice structure of clay minerals and some properties of clays. *Jour. Geol.* 50: 276-290.
- (9) JENNY, H., AND AYERS, A. D. 1939 Influence of the degree of saturation of soil colloids on the nutrient intake by roots. *Soil. Sci.* 48: 443-459.
- (10) KUNIN, R., AND MYERS, R. J. 1950 Ion Exchange Resins. John Wiley and Sons, Inc. New York.
- (11) MARSHALL, C. E. 1943 Use of membrane electrodes in the study of soils. *Soil Sci. Soc. Amer. Proc.* (1942) 7: 182-186.
- (12) MARSHALL, C. E. 1948 Ionization of calcium from soil colloids and its bearing on soil-plant relationships. *Soil Sci.* 65: 57-68.
- (13) MARSHALL, C. E. 1949 Colloid Chemistry of the Silicate Minerals. Academic Press, Inc., New York.
- (14) MATTSON, S. 1932 Laws of soil colloidal behavior: IX. *Soil Sci.* 34: 209-240.
- (15) MEHLICH, A., AND COLWELL, W. E. 1944 Influence of nature of soil colloids and degree of base saturation on growth and nutrient uptake by cotton and soybeans. *Soil Sci. Soc. Amer. Proc.* (1943) 8: 179-184.
- (16) MEHLICH, A. 1946 Soil properties affecting the proportionate amounts of calcium, magnesium, and potassium in plants and in HCl extracts. *Soil Sci.* 62: 393-409.
- (17) MEHLICH, A., AND REED, J. F. 1948 Effect of cation-exchange properties of soil on the cation content of plants. *Soil Sci.* 66: 289-306.
- (18) MEHLICH, A. 1948 Determination of cation and anion exchange properties of soils. *Soil Sci.* 66: 429-445.
- (19) MEHLICH, A. 1950 Cation exchange-anion exchange ratios of kaolinitic soil colloids. *Trans. 4th Internatl. Cong. Soil Sci.* 1: 133-135.
- (20) MUKHERJEE, J. N., CHATTERJEE, B., AND BANNERJEE, B. M. 1947 Liberation of H, Al, and Fe ions from hydrogen clays by neutral salts. *Jour. Colloid Sci.* 2: 247-256.

- (21) PAVER, H., AND MARSHALL, C. E. 1934 Role of aluminum in the reactions of the clays. *Chem. and Indus.* 12: 750-760.
- (22) PRESCOTT, J. A., AND ARTHUR, J. I. 1945 Ultimate pH value of the soil and its relation to the composition of the clay fraction. *Jour. Aust. Inst. Agr. Sci.* 9: 125-127.
- (23) SCHUYLENBORGH, J. 1950 Electrokinetic behavior of the sesquioxide hydrates and its bearing on the genesis of clay minerals. *Trans. 4th Internatl. Cong. Soil Sci.* 1: 89-92.

ACCUMULATION OF THE MAJOR BASES AND HEAVY METALS IN FLORIDA CITRUS SOILS IN RELATION TO PHOSPHATE FERTILIZATION

WALTER REUTHER, PAUL F. SMITH, AND ALSTON W. SPECHT

U. S. Department of Agriculture¹

Received for publication July 26, 1951

A previous paper (12) reported that the rate of phosphate fertilization had little effect on the exchangeable base status of soil in an experimental Valencia orange orchard in Florida. The rate of phosphate fertilization was also shown to affect only slightly the concentration of phosphorus and the major bases in the foliage. It sharply increased the concentration of zinc and manganese and decreased the concentration of copper in leaves.

The present paper summarizes the results of total analyses of topsoil samples collected at the outset of the experiments and after about 7 years of differential phosphate treatment. These samples were obtained from the aforementioned experimental orchard and from similar long-term field experiment with Pineapple oranges in which the rate of superphosphate fertilization is the major variable. These data are concerned with the accumulation in the soil of applied nutrient cations and its relation to the rate of phosphate fertilization.

EXPERIMENTAL METHODS

Details of the plan of the two phosphate experiments were given in a previous report (12). Briefly, three levels of superphosphate fertilization and a no-phosphate treatment are being compared in a mature Valencia orange orchard and in a young Pineapple orange orchard. Treatment of the latter was begun at the time of planting on virgin soil. Accurate records have been kept of the amounts of elements applied in fertilizers to all plots since the beginning of the experiments. Sulfates of copper, manganese, and zinc were generally included in the nonphosphatic mixed fertilizer applied uniformly to all plots.

Topsoil samples were collected from the plots before differential treatment was started and at intervals thereafter. Each sample was a composite of 12 to 18 cores per plot obtained with a 1-inch steel tube in the area just beyond the outer branches of the central trees.

Total assays were made on samples by digesting 10 gm. of air-dry soil in a small pyrex volumetric flask with 3 ml. of concentrated H_2SO_4 and 2 to 3 ml. of concentrated HNO_3 and heating on a hot plate until organic matter was completely destroyed. Total copper, zinc, and manganese were determined directly on aliquots of this digest (suitably diluted) by AOAC methods (1). Total phosphorus was estimated on aliquots of a greater dilution of this digest by the method of Cotton (3). Total calcium and manganese were determined on small aliquots of this digest by a spectrographic method (4), and total potassium was determined by the flame method, using a quartz spectrophotometer (2).

¹ U. S. Subtropical Fruit Field Station, Orlando, Florida.

RESULTS

The data in table 1 show that heavy applications of superphosphate and the resulting accumulation of phosphatic materials in the topsoil of these two citrus orchards did not profoundly influence the level of total major bases in the topsoil. The data suggest that heavy phosphate fertilization was associated with slightly higher total potassium and lower total magnesium in the topsoil

TABLE 1

Effect of about 7 years of differential phosphate treatment on total phosphorus, bases, and heavy metals in the topsoil of two experimental orange orchards

TREATMENTS AND STATISTICAL INDEXES	SOIL ANALYSIS†						
	P	Ca	Mg	K	Mn	Cu	Zn
<i>Valencia plots—1949 samples, 0-9 inches</i>							
A—No P_2O_5	755	5100	490	179	205	156	107
B—Low P_2O_5	914	5450	577	168	225	180	—
C—Medium P_2O_5	1061	5170	513	186	210	172	—
D—High P_2O_5	1471	5040	386	191	191	169	108
Effect of treatment.....	**	N.S.	*	N.S.	N.S.	N.S.	N.S.
L.S.D. at 0.05.....	216	—	103	—	—	—	—
S.E. of means.....	70	230	34	13	18	9.4	—
<i>Pineapple plots—1950 samples, 0-6 inches</i>							
A—No P_2O_5	515	6940	186	132	126	51	22
B—Low P_2O_5	544	7700	186	158	134	49	—
C—Medium P_2O_5	549	6630	195	164	126	44	—
D—High P_2O_5	738	6930	176	186	126	56	21
Effect of treatment.....	**	N.S.	N.S.	**	N.S.	N.S.	N.S.
L.S.D. at 0.05.....	91	—	—	23	—	—	—
S.E. of means.....	30	840	16	7.7	6	3	—

† Mean of five and six replicates per treatment, respectively; in pounds per acre air-dry soil. Statistical symbols:

* Analysis of variance indicates effect of treatment is significant by odds of more than 19:1.

** Analysis of variance indicates effect of treatment is significant by odds of more than 99:1.

N.S. No significant effect of treatment.

L.S.D. at 0.05: least difference for significance between any two means with odds of 19:1.

S.E. of means: standard error of treatment means.

but are not sufficiently consistent or clear-cut in both locations to warrant definite conclusions. Similarly, the rate of phosphate fertilization did not appear to affect total copper, manganese, or zinc in the topsoil.

The "percentage retained" figures in table 2 should be taken as being indicative only, since the error in sampling field plots is large (note standard error values in table 1). This is due largely to normal soil heterogeneity and to the uneven distribution of applied fertilizers in ordinary orchard practice. For

example, the data in table 2 suggest that in some cases there was a greater gain in heavy metal content than could be accounted for by fertilizer application. The amounts applied were calculated on the basis of uniform distribution to the plot area, though fertilizer applied by machine to the Valencia plots tended to deposit more heavily around the "drip" of the tree and in the middles, at the expense of the soil area under the spread of the branches in this closely planted mature orchard with low "skirts." The total copper content in six

TABLE 2

Changes in total base and heavy metal contents of the topsoil in two series of phosphate plots during a 7-year period

DATES AND MEASURES	SOIL ANALYSIS*						MEDIAN pH
	Ca	Mg	K	Mn	Cu	Zn	
<i>Valencia plots†</i>							
Apr. 1942 samples.....	3280	231	186	49	17	30	5.7
Nov. 1949 samples.....	5190	492	179	207	170	107	5.1‡
Gain, 1942 to 1949.....	1910	261	—7	158	153	77	—
Applied, 1942 to 1949.....	3870	792	1370	127	122	68	—
% of applied retained.....	50	33	loss	124	125	115	—
<i>Pineapple plots§</i>							
Virgin samples.....	9070	184	124	95	5	13	5.8
Jan. 1950 samples.....	7050	185	160	128	50	21	5.4
Gain, 1943 to 1950.....	—2020	1	36	33	45	8	—
Applied, 1943 to 1950.....	1070	405	323	62	33	9	—
% of applied retained.....	loss	0	11	53	136	89	—

* Each value represents the pooling of all treatments from 20 or 24 plots; in pounds per acre air-dry soil.

† The 1942 samples were taken to an empirical depth of 0-12 inches, and hence calculated on the basis of 4×10^6 pounds per acre. The 1949 samples were of the A horizon only, and averaged 0-9 inches in depth, and hence calculated on the basis of 3×10^6 pounds per acre.

‡ About $4\frac{1}{2}$ pounds NH_4NO_3 per tree applied 3 weeks before samples were collected, and hence pH probably temporarily depressed below previous level.

§ All samples taken of A horizon (0-6 inches average) and calculated on the basis of 2×10^6 pounds per acre. The virgin samples were collected in 1945 from the unfertilized middles, and were taken to approximate the virgin status of the soil when planted in 1943.

soil samples obtained in these Valencia plots from under the trees was about half that in corresponding samples obtained from the area just outside the spread of the branches. In view of these limitations, small effects or slight trends cannot be determined with certainty from these data.

Table 2 indicates the changes during the 7-year period. The total potassium and the total magnesium status of the soil were not greatly altered by application of these elements during the experimental period. Evidently, the portions of these elements not taken up by the tree were leached out of the topsoil, and hence there was no appreciable tendency to accumulate. There was an ap-

preciable buildup of calcium in the Valencia plots during the experimental period, but a considerable loss in the Pineapple plots, although the rate of loss was about the same in both locations. The heavy metals, on the other hand, had a strong tendency to accumulate. For example, the total copper content of the topsoil in both experimental orchards increased about ninefold during the 7-year period. Zinc and manganese increased twofold to threefold during this period in the Valencia plots but less in the Pineapple plots because less was applied. The proportion of applied heavy metals retained by the topsoil was roughly of the same order of magnitude for all three cations at both locations.

DISCUSSION AND CONCLUSIONS

Under the orchard conditions considered, the level of superphosphate and its reversion products in the soil had no profound and consistent effect on the level of total major bases in the soil or on the retention of applied copper, manganese, and zinc. This is substantially in agreement with the laboratory findings of Jamison (9) and Erwin (6) with respect to the effect of added phosphates on the retention of copper and zinc by soils of this type. In laboratory tests with virgin sandy soil, typical of that used for citrus in the Ridge section of Florida, Wander (15) showed, however, that adding calcium phosphate precipitated at pH 6.0 increased the capacity to retain manganese and magnesium added as neutral salts, but had no influence on the retention of added potassium. Furthermore, Wander postulated that phosphate compounds, which are known to accumulate in Florida orchard soils as a result of systematic application of phosphate-rich mixed fertilizers and liming materials, tend to reduce leaching loss of magnesium and manganese, but not potassium, added as neutral salts. He suggested that this absorptive capacity of the accumulated calcium phosphate improves the nutrition of citrus in sandy soils of low exchange capacity. The long-term lysimeter investigations of MacIntire *et al.* (11) indicated that, with several acid soils studied, addition of monocalcium and other calcium salts of phosphate, with or without liming, tends to reduce slightly the leaching loss of both magnesium and potassium. In studies with calcium-rich soil, added ammonium phosphate or ammonium sulfate tended to stimulate leaching of magnesium and calcium but did not affect potassium loss. The studies of Davis (5) on an acid sandy loam of Louisiana showed that additions of both lime and monocalcium phosphate produced an increase in cation-exchange capacity under laboratory conditions, and that the change produced by liming was relatively large compared with that produced by phosphate. The studies of Haseman *et al.* (7, 8) suggested that potassium (and phosphate) may be fixed in soils as potassium aluminum phosphate. Although our data suggested that a small quantity of potassium may be fixed by phosphates, this type of fixation is apparently of little significance under these orchard soil conditions.

Thus, evidence from several sources indicates that phosphatic materials added to acid, humid-region soils may increase the retention of cations under certain conditions. Whether the higher level of accumulated phosphate in the

limed field plots with grapefruit, as compared with the very acid unlimed plots studied by Wander (15), was a major factor in the greater vigor and higher yield is still an open question, in our opinion. In our studies (12) with well-replicated field plots on soils similar to the type studied by Wander, but with the level of accumulated phosphate in the soil as the primary variable and soil pH and liming treatment relatively constant factors, no benefit to yield or vigor was observed to be associated with higher total phosphate level. This suggests that the growth and yield effects observed by Wander were probably due primarily to other favorable nutrient factors produced by liming (14) rather than to the added adsorptive capacity associated with the higher level of accumulated phosphate induced by liming.

Leaf analysis data for two seasons from our phosphate plots have been published (12). Additional leaf analysis data (unpublished) on the major bases in comparable samples obtained from these plots during the last three seasons confirm the trends suggested by the published data. Heavy phosphate fertilization was associated with slightly to moderately increased calcium content of the foliage in all five seasons observed in the Pineapple plots and in four seasons of the five in the Valencia plots. Depressed magnesium content of the foliage was associated with heavy phosphate fertilization in all five seasons in both locations. Despite these consistent trends, in most seasons heavy phosphate fertilization did not affect potassium concentration in the foliage, but in a few seasons there was a slight tendency toward depression. It appears, then, that heavy fertilization of limed soil with superphosphate tends to increase slightly the level of calcium in leaves and to decrease magnesium without markedly influencing the total quantity of these elements in the topsoil. This suggests that monocalcium and other calcium salts of phosphate tend to increase calcium availability in the soil. Likewise, the higher concentrations of zinc and manganese and the lower concentration of copper observed in the foliage of Valencia trees receiving heavy phosphate treatment (12) are not related to the total quantity of these elements in the topsoil. They are related, apparently, to some differential effect of heavy fertilization with superphosphate on availability in the soil or uptake by roots.

Perhaps the conclusion with potentially the greatest implications for orchard practice is that these data confirm, under orchard conditions, the high fixing capacity of soils like the Lakeland series for copper and zinc indicated by laboratory studies (6, 9, 10) and suggest that manganese also belongs to this group. It is apparent that the practice, common during the last decade in Florida, of systematically applying these elements in mixed fertilizers or foliage sprays to citrus orchards on this type of soil will result in gradual accumulation of large quantities of these heavy metals in the soil. In 1942, the copper, zinc, and manganese accounted for about 2.5 per cent of the total cation content of the topsoil from the Valencia plots, if iron and aluminum are ignored. By 1949, they accounted for about 7.5 per cent of the total cation content. In comparison with the total potassium, topsoil from the Valencia plots in 1949 (table 1) contained somewhat more total manganese, about the same amount of total cop-

per, and only slightly less zinc. Since topsoil of this type contains only 3 or 4 per cent of colloidal material (mostly organic matter), the rest being sand (13), the concentrations of these heavy metals would be much higher if expressed on the basis of the active part of the soil.

The spectrographic analyses of Rogers *et al.* (13) of topsoil samples from 28 citrus orchards on the Lakeland (formerly called Norfolk) series, presumably collected during 2 or 3 years prior to 1939, showed that the majority ranged from 2 to 60 pounds per acre-6-inches for total copper and manganese and from 16 to 160 pounds for zinc. The majority of the values for 11 comparable virgin soil samples were 2 to 20 pounds for copper and 2 to 60 for manganese and zinc. Topsoil samples collected by the authors in 1948 and 1949 from 14 citrus orchards, all more than 20 years old, ranged from 86 to 450 pounds of total copper per acre-6-inches, with most values above 200 pounds per acre. How high the levels of these heavy metals must become before the uptake of other nutrients is disturbed, or toxicity to citrus is induced, is currently being investigated at this laboratory.

SUMMARY

This paper is concerned with the trend of total calcium, magnesium, potassium, copper, manganese, and zinc in soil from two long-term field phosphate experiments with oranges in Florida. Three levels of superphosphate and a no-phosphorus treatment are compared in two experimental orchards on acid, sandy soil. Soil analyses before and after 7 years of differential treatment show that heavy phosphate fertilization, and the resulting accumulation of phosphate, did not greatly influence the accumulation of cations. There was a suggestion, however, that total potassium was slightly increased, while total magnesium was slightly decreased by heavy phosphate fertilization. The magnitude of these trends was not great enough to be of much significance to soil fertility. The data showed that high proportions of the elements copper, manganese, and zinc applied to such orchard soil were retained in the topsoil, irrespective of phosphate treatment. A question is raised concerning the potential significance of the gradual accumulation of these heavy metals in citrus orchard soil.

REFERENCES

- (1) Association of Official Agricultural Chemists. 1945 Official and Tentative Methods of Analysis, ed. 6. Washington, D. C.
- (2) BROWN, J. D., LILLELAND, O., AND JACKSON, R. K.: 1950 Further notes on the use of flame methods for analysis of plant materials for K, Ca, Mg, and Na. *Amer. Soc. Hort. Sci. Proc.* 56: 12-22.
- (3) COTTON, R. H. 1945 Determination of nitrogen, phosphorus, and potassium in leaf tissue. *Indus. and Engin. Chem., Analyt. Ed.* 17: 734-738.
- (4) CURRAN, H. R., BRUNSTETTER, B. C., AND MYERS, A. T. 1943 Spectrochemical analysis of vegetative cells and spores of bacteria. *Jour. Bact.* 45: 485-494.
- (5) DAVIS, F. L. 1945 Retention of phosphates by soils: II. *Soil Sci.* 59: 175-190.
- (6) ERWIN, T. C. 1945 Leaching and availability of copper as affected by phosphorus and lime. *Soil Sci. Soc. Fla. Proc.* 7: 49-57.
- (7) HASEMAN, J. F., BROWN, E. H., AND WHITT, C. D. 1950 Some reactions of phosphate with clays and hydrous oxides of iron and aluminum. *Soil Sci.* 70: 257-271.

- (8) HASEMAN, J. F., LEHR, J. R., AND SMITH, J. P. Mineralogical character of some iron and aluminum phosphates containing potassium and ammonium. *Soil Sci. Soc. Amer. Proc.* (1951) (in press).
- (9) JAMISON, V. C. 1944 Effect of particle size of copper and zinc source materials and of excessive phosphates upon the solubility of copper and zinc in a Norfolk fine sand. *Soil Sci. Soc. Amer. Proc.* (1943) 8: 323-326.
- (10) JONES, H. W., GALL, O. E., AND BARNETTE, R. M. 1936 Reaction of zinc sulfate with the soil. *Fla. Agr. Exp. Sta. Bul.* 298: 1-42.
- (11) MACINTIRE, W. H., SHAW, W. M., AND ROBINSON, B. 1949 Migrations of phosphorus and other elements from variously phosphated soils, with and without calcium fluoride and liming materials. *Soil Sci.* 67: 377-394.
- (12) REUTHER, W., et al. 1949 Phosphate fertilizer trials with oranges in Florida: I. *Amer. Soc. Hort. Sci. Proc.* 53: 71-84.
- (13) ROGERS, L. H., et al. 1939 Distribution of macro and micro elements in some soils of peninsular Florida. *Fla. Agr. Exp. Sta. Bul.* 341: 1-31.
- (14) SCHMEHL, W. R., PEECH, M., AND BRADFIELD, R. 1950 Causes of poor growth of plants on acid soils and beneficial effects of liming: I. *Soil Sci.* 70: 393-410.
- (15) WANDER, I. W. 1950 Effect of calcium phosphate accumulation in sandy soil on the retention of Mg and Mn and the resultant effect on the growth and production of grapefruit. *Amer. Soc. Hort. Sci. Proc.* 55: 81-91.

LEACHING OF CALCIUM IN A FINE SANDY LOAM AS INDICATED BY Ca45

JAMES M. BLUME

U. S. Department of Agriculture¹

Received for publication September 14, 1951

Radioisotopes are convenient tools for measuring the movement of fertilizer elements from placement sites in the soil, although their use for this purpose appears to have been largely neglected. In plans for the use of Ca45 in a field experiment, information was needed on the depth to which calcium from an application of a salt might penetrate the soil under the influence of severe leaching. Since such data were not available, laboratory studies were carried out. The methods and results of two such experiments are reported here.

GENERAL METHODS

The procedure was to prepare soil columns, each of which contained a Ca45-labeled calcium compound in an upper layer, leach the columns with the desired volumes of water, and then analyze the leachates and the various layers of the columns for Ca40 and Ca45.

The columns were prepared in plastic tubes $4\frac{9}{16}$ inches inside diameter and 17 inches long. The component parts of the apparatus and the method of sampling after leaching are shown in figure 1. Lucite was chosen as the material for the tubes because it is not wetted by water, and thus there is little tendency for water to flow down the tube walls in preference to passage through the soil pores. In filling the tubes, soil was added in 600-gm. increments, each successive increment being moistened to near the saturation point before further addition of soil. All water used in the experiments had been demineralized by passage through ion-exchange columns. The radioactive calcium was procured from the Isotopes Division of the U. S. Atomic Energy Commission and was listed in their catalog as Item S5-B.

The sample slices of soil removed after leaching were air-dried and passed through a 2-mm. sieve. One hundred-gram samples of the soil were then extracted with 1 liter of neutral normal ammonium acetate (4). The calcium was precipitated as the oxalate, which was collected on tared filter paper disks.² Ca40 was determined gravimetrically and the relative Ca45 content by counting the calcium oxalate precipitates with an end-window Geiger tube (window thickness 2.4 mgm./cm²). Counts were corrected for self-absorption. Decay corrections were unnecessary, since counts for an entire experiment could be made in 3 or 4 days. Ca40 and Ca45 determinations on the water leachates were made by the methods indicated for the ammonium acetate extracts.

The soil used in the study was a Norfolk fine sandy loam from near Raleigh, N. C. Some of its characteristics are given in table 1.

¹ This investigation was supported in part by the U. S. Atomic Energy Commission.

² Borland, J. W., Schmehl, W. R., Peech, M., and Reitemeier, R. F. (To be published in *Analyt. Chem.*)

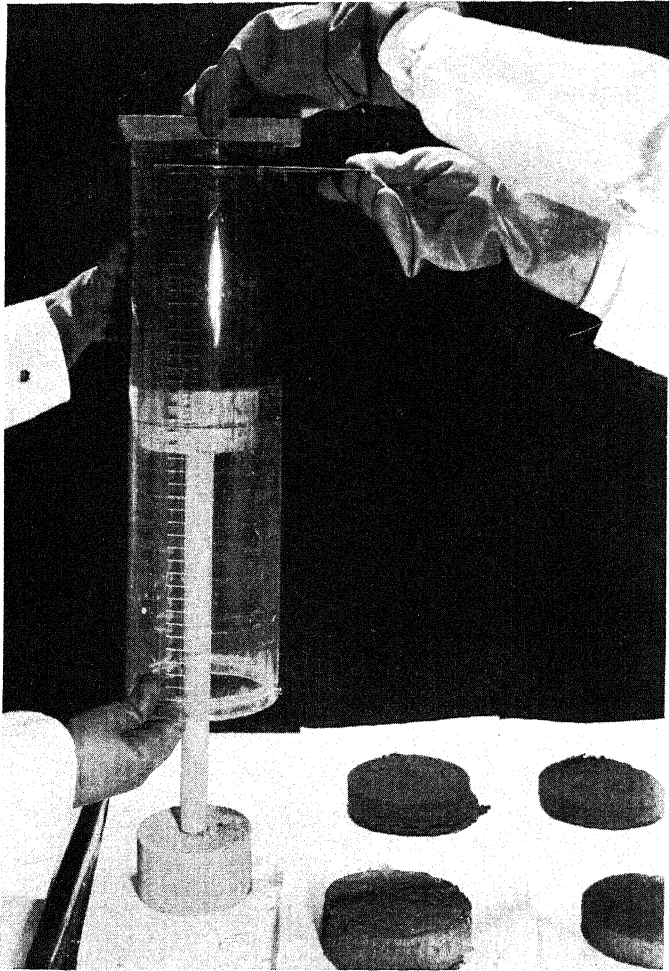


FIG. 1. SAMPLING COLUMN OF SOIL AFTER LEACHING

TABLE 1
Characteristics of Norfolk fine sandy loam

EXCHANGEABLE CATIONS		U.S.D.A. PARTICLE SIZE	
	<i>me./100 gm.</i>		<i>per cent</i>
H.	4.7	Very coarse sand	8.0
Ca.....	1.9	Coarse sand.....	19.4
Mg.....	0.2	Medium sand.....	14.0
K.....	0.2	Fine sand.....	22.2
Na.....	0.1	Very fine sand.....	12.0
Mn.....	tr.	Silt.....	18.4
Exchange capacity (sum).....	7.1	Clay.....	6.0

EXPERIMENT I

In the first experiment four treatments differed from one another in the amount and carrier of the labeled calcium of the treated soil layers. In all four treatments the labeled layer, which was 4 cm. thick (600 gm. air-dried soil),

TABLE 2
Cumulative leaching of calcium from columns of Experiment I

LEACHING	TOTAL Ca IN LEACHATES				L.S.D.	
	Normal soil	Ca(OH) ₂	CaSO ₄ ·2H ₂ O	CaCO ₃	5%	1%
<i>in.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>		
3.20*	60.4	64.1	51.5	71.3	5.6	8.0
6.59*	74.2	77.9	88.7	85.5	5.7	8.1
9.77*	87.4	92.0	109.5	98.1	5.3	7.6
16.25*	111.7	114.9	136.3	119.7	4.9	7.0
26.42†	147.5	145.8	168.3	146.8	13.0	—
40.77†	200.7	195.6	211.5	183.5	15.9	—

* Mean of four replications.

† Mean of two replications.

rested on 20 cm. of untreated soil and was covered by 3 cm. of untreated soil. The soil for the treated layers was prepared as follows:

Normal soil. The calcium of the exchange complex was labeled by treating a suspension of 3 parts soil in 1 part water with a solution of CaCl₂ containing Ca45. After being stirred, the mixture was allowed to dry at room temperature. The soil was resuspended in the same quantity of water as before, dried at room temperature, suspended in water a third time, again dried, and finally passed through a 2-mm. sieve. The total amount of calcium added in the labeling process amounted to less than 0.5 per cent of the exchangeable calcium originally present.

Ca(OH)₂ treatment. Labeled Ca(OH)₂, as a saturated solution, was added to the soil at a rate sufficient to provide 250 pounds Ca per acre (area basis). Equilibration and drying were carried out as previously described, after which the added calcium was assumed to be present as part of the exchange complex.

CaSO₄·2H₂O treatment. Labeled gypsum, equivalent to 250 pounds Ca per acre (area basis), was dry mixed with the soil, water being added as the columns were made up.

CaCO₃ treatment. Labeled CaCO₃, equivalent to 250 pounds Ca per acre (area basis) was dry mixed with the soil, water being added as the columns were made up.

After preparation of the columns, they were allowed to stand in a vertical position for 2 days before leaching was initiated. Water was then added at the rate of 500 ml. (1.84 inches) per tube on each of two successive mornings, followed by no water on the third day. This pattern was repeated throughout the course of the experiment. Two replicate columns of each treatment were leached with 16.25 inches of water, disassembled, and sampled. The remaining two replicates were leached with 40.77 inches of water before sampling.

All leachings were collected in fractions of approximately 1 liter each and analyzed for total calcium and Ca45. Table 2 gives the condensed results of the total calcium analyses. No Ca45 was detected in any of the leachates.

After cessation of leaching, each column was cut into transverse slices 2 cm. thick, although not all slices were retained for analysis. The sample taken from the original 4-cm. treated layer was a 2-cm. slice from its middle. The next 2-cm. slices on each side, which covered the transition zones between treated and untreated soil, were discarded. Table 3, which concerns the movement of the labeled calcium, indicates the vertical distribution of the slices analyzed.

TABLE 3
Movement of calcium from treated layer in Experiment I

LOCATION IN COLUMN	Ca45 IN RELATIVE COUNTS*			
	Normal Soil	Ca(OH) ₂	CaSO ₄ ·2H ₂ O	CaCO ₃
<i>16.25 inches of leaching</i>				
Above treated layer				
1-3 cm.....	0.0	0.0	0.0	0.0
Middle 2 cm. of treated layer...	97.3 ± 1.5†	92.8 ± 3.9	61.6 ± 6.5	94.2 ± 0.3
Below treated layer				
1-3 cm.....	2.7 ± 0.0	7.2 ± 1.4	32.8 ± 1.3	5.8 ± 2.0
5-7 cm.....	0.0	0.0	6.1 ± 3.9	0.0
11-13 cm.....	0.0	0.0	0.0	0.0
<i>40.77 inches of leaching</i>				
Above treated layer				
1-3 cm.....	0.0	0.0	0.0	0.0
Middle 2 cm. of treated layer...	94.1 ± 3.8	66.7 ± 1.5	52.5 ± 2.0	77.1 ± 3.6
Below treated layer				
1-3 cm.....	5.9 ± 3.1	33.0 ± 4.9	36.1 ± 0.3	22.9 ± 4.3
5-7 cm.....	0.0	0.3 ± 0.3	11.4 ± 1.6	0.0
11-13 cm.....	0.0	0.0	0.0	0.0

* Mean of duplicate columns.

† Standard error.

EXPERIMENT II

In the second experiment, the following materials were incorporated into a 1-cm. layer resting on 33 cm. of untreated soil and covered with 4 cm. of untreated soil: 1.13 gm. (NH₄)₂SO₄, 0.49 gm. CaH₄(PO₄)₂·H₂O, 0.49 gm. CaSO₄·2H₂O, and 0.23 gm. KCl. These materials provided 200 pounds N, 100 pounds P, and 100 pounds K per acre, all on an area basis. The gypsum was approximately equal to the calcium sulfate which would have been present in the quantity of 18-20 per cent superphosphate needed to supply 100 pounds P per acre.

In half of the columns the monocalcium phosphate was labeled with Ca45; in the other half, the gypsum was tagged. Two replicates of each of the treatments were planted to oats, which were harvested after 30 days. The remaining two replicate columns were fallow during the 30 days, the moisture content being adjusted weekly to the approximate level present at the beginning of the

experiment. After the 30-day period, the columns were leached with 17.47 inches of water, as previously described. They were then disassembled and sampled.

Insofar as the leaching of calcium from the tubes and distribution of total calcium within the columns is concerned, there were only two treatments; namely, planted and fallowed. Table 4 gives the amounts of calcium leached from the columns. Table 5 indicates the vertical distribution of calcium within

TABLE 4
Removal of calcium in successive leachates in Experiment II

WATER		Ca LEACHED PER COLUMN		L.S.D. 1%
Individual leaching	Cumulative total	Planted	Fallow	
<i>in.</i>	<i>in.</i>	<i>mgm.</i>	<i>mgm.</i>	
3.35	3.35	101.9	264.5	63.4
3.56	6.91	33.3	44.2	n.s.
3.55	10.46	11.9	10.5	n.s.
3.49	13.95	8.4	5.1	1.3
3.52	17.47	10.1	5.0	4.9
Total		165.6	329.3	36.8

TABLE 5
Exchangeable calcium after leaching, Experiment II

LOCATION IN COLUMN	Ca PER 100 GM. SOIL	
	Planted	Fallowed
	<i>mgm.</i>	<i>mgm.</i>
Above treated layer		
½ to 2½ cm.	33.4	32.4
Treated layer plus		
½ cm. above and ½ cm. below	38.3	34.9
Below treated layer		
½ to 2½ cm.	36.4	32.7
4½ to 6½ cm.	34.7	33.8
8½ to 10½ cm.	42.6	40.3
12½ to 14½ cm.	44.0	42.6
18½ to 20½ cm.	43.1	41.8

the columns. With respect to movement of calcium from the labeled compounds, there were four treatments; namely, $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ tagged, column planted; $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ tagged, column fallowed; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ tagged, column planted; and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ tagged, column fallowed. Because of the exchange of calcium which may occur between the monocalcium phosphate and the gypsum, the Ca45 cannot be identified as completely belonging to either compound after the two are mixed and placed in the soil. The Ca45 counts, then, which are reported in table 6, give the relative concentration of Ca45 at various depths

after leaching, but should not be considered as indicating relative depth of penetration of calcium from gypsum and monocalcium phosphate.

TABLE 6
Movement of calcium from treated layer in Experiment II

LOCATION IN COLUMN	Ca45 IN RELATIVE COUNTS*			
	Planted		Fallowed	
	CaSO ₄ ·2H ₂ O	CaH ₄ (PO ₄) ₂ ·H ₂ O	CaSO ₄ ·2H ₂ O	CaH ₄ (PO ₄) ₂ ·H ₂ O
Above treated layer				
½-2½ cm.....	1.3	0.9	3.5	5.6
Treated layer plus				
½ cm. above and below.....	54.1	37.8	48.3	42.2
Below treated layer				
½-2½ cm.....	32.2	40.3	34.5	35.2
4½-6½ cm.....	7.4	14.1	11.5	12.1
8½-10½ cm.....	4.8	6.1	2.1	4.6
12½-14½ cm.....	0.2	0.8	0.1	0.3
18½-20½ cm.....	0.0	0.0	0.0	0.0

* Means of duplicate columns.

DISCUSSION

Movement of the calcium from the treated layer was surprisingly small in both experiments, even though an appreciable fraction of the total exchangeable calcium in the soil was lost to the leachates. In the first experiment, approximately 14 per cent of the calcium was leached from the column designated as "normal soil" by 40.77 inches of water. None of the calcium from the tagged layer moved down as much as 5 cm. under the influence of this amount of leaching. Only a trace of Ca45 was found in the 5-7-cm. layer of the Ca(OH)₂ treatment, whereas none penetrated this far in the CaCO₃ treatment. The greatest extent of Ca45 movement was with the gypsum treatment, 11.4 per cent of the recovered Ca45 appearing in the 5-7-cm. layer. None penetrated as far as 11 cm. When large amounts of soluble salts were incorporated in the treatment layer (Experiment II), more of the applied calcium moved from the original zone of application, but the greatest distance to which any of the Ca45 moved was but little more than that in the absence of additional fertilizer salts, only traces being found in the sample taken at 12½-14½ cm. below the treated layer.

In Experiment II, considerably more calcium was leached from the fallowed columns than from the cropped columns by the first 3.35 inches of leaching. With the second and third liters of leaching, the differences between cropped and fallowed soil were small. Finally, with the last 2 liters of water, the pattern was reversed, the cropped soil losing significantly more calcium than the fallowed soil. This reversal of trend is a reflection of the lower calcium content of the fallowed soil as a consequence of the heavy early removals. It is likely that the increased leaching of calcium from the fallowed tubes by the first liter of water was due largely to the influence of nitrate formed from the ammonium ion by microbial oxidation. Although the presence of sulfates and chlorides also may have been a factor (1), there is no reason to think that the concentra-

tions of these ions differed greatly between cropped and uncropped soils, while nitrate undoubtedly accumulated in the fallowed soil as compared to the cropped soil. Volk and Bell have shown that calcium moves predominantly as the nitrate, when this anion is present (5). Morgan and his associates reported large losses of calcium from soils fertilized with ammonium sulfate (2), and in other lysimeter studies they found greater leaching of calcium from uncropped than from cropped soils (3).

A net loss of calcium occurred principally from the upper layers of the columns. Although the introduction of the slices of treated soil with a higher total calcium content into the upper parts of the tube complicated the picture somewhat by preventing a smooth gradient in calcium from top to bottom, the extreme upper layer in every case contained less exchangeable calcium than did any of the lower layers. In treatments where large amounts of soluble fertilizer salts had been applied (Experiment II), there was a second zone of lowered exchangeable calcium content immediately below the treated layer. In these treatments the lowest layers of the columns contained more exchangeable calcium after leaching than before, because of movement from the upper layers.

These data suggest that when a soil is leached, the calcium moves as a front, a portion from one layer displacing some of that from the layer immediately below, no individual calcium atom moving very far. As this process continues under sustained leaching, the soil layers at the extreme top of the column are depleted of calcium, but it is calcium from the layers at the bottom of the column that actually enters the leachate.

SUMMARY

Experiments dealing with the movement of calcium in Norfolk fine sandy loam under the influence of severe leaching were carried out in the laboratory with the aid of Ca^{45} . The distance calcium moved from a particular layer was slight, even when the total amount of calcium leached from a soil was appreciable. Apparently, calcium moved down the column by a continuous series of displacements, the calcium appearing in the leachates being that originally present in the lower layers of the soil. The total amount of calcium leached from a heavily fertilized soil was greater when the soil had been fallowed than when cropped, although the distance any particular calcium atom moved was not affected.

REFERENCES

- (1) JACOBSON, H. G. M., SWANSON, C. L. W., AND SMITH, E. 1948 Effect of various fertilizer cations and anions on soil reaction, leaching, nitrification of urea, and related characteristics in an uncropped soil. *Soil Sci.* 65: 437-460.
- (2) MORGAN, M. F., AND JACOBSON, H. G. M. 1942 Soil and crop interrelations of various nitrogenous fertilizers. Conn. Agr. Expt. Sta. Bul. 458.
- (3) MORGAN, M. F., JACOBSON, H. G. M., AND Lecompte, S. B., JR. 1942 Drainage water losses from a sandy soil as affected by cropping and cover crops. Conn. Agr. Expt. Sta. Bul. 466.
- (4) PEECH, M., et al. 1947 Methods of soil analysis for soil-fertility investigations. U. S. Dept. Agr. Cir. 757.
- (5) VOLK, G. M., AND BELL, C. E. 1945 Some major factors in the leaching of calcium, potassium, sulfur, and nitrogen from sandy soils. Fla. Agr. Expt. Sta. Bul. 416.

DETERMINATION OF SOIL MOISTURE BY NEUTRON SCATTERING

WILFORD GARDNER AND DON KIRKHAM

*Iowa State College*¹

Received for publication September 17, 1951

A number of methods for determining soil moisture are available. The most common method is that of weighing a sample before and after oven-drying. Other methods are not so direct. In them, a soil characteristic other than its moisture content is measured. Some characteristics that have been utilized are electrical and thermal conductivity, thermal diffusivity, dielectric constant, and moisture tension. None of these methods has been completely satisfactory. In the oven-drying method, the sample is changed in the measuring process; continuous readings of the moisture at a point in the soil cannot be made. In the indirect methods, calibrations are required, and they are not dependent alone on the moisture content of the soil. Some of the factors that may disturb calibrations are texture, temperature, electrical contact resistance, salt concentration, and time of reading. Time of reading causes trouble in methods in which a period of time is required for the soil moisture detector to come into equilibrium with the surrounding water. Salt concentrations bother when fertilizer is added to soils under investigation. Also salt concentration in soil may change as a consequence of evaporation.

An approach to a soil-moisture measuring technique that would seem to obviate some of the aforementioned difficulties might be the use of emanations from radioactive materials. Alpha, beta, and gamma rays and neutrons come to mind.

Gamma rays have been used successfully for measuring the quantity of water stored in a snow pack (5). In this case a beam of the rays is passed through the pack. The intensity of radiation getting through the pack from a source of known intensity yields a measure of the water content.

Application of gamma rays to the determination of soil moisture would probably be unsatisfactory. The solid material in the soil would absorb the radiation much as does water. Water could not be differentiated from other soil elements. Furthermore, the extremely long range of gamma rays would make them undesirable. The ranges of alpha and beta rays, on the other hand, are too short to seem practical.

The use of neutrons seems more promising.² In well logging (3) a source of

¹ Journal Paper J-2007 of the Iowa Agricultural Experiment Station, Ames, Project 998, in cooperation with the Physics Department. The authors thank G. W. Fox and members of the Iowa State College Institute for Atomic Research; in particular, D. S. Martin, for advice and help.

² After principal results presented in this paper were obtained, a report on the use of neutron scattering for determining soil moisture was published by the Technical Development and Evaluation Center of the Civil Aeronautics Administration, Indianapolis, as

neutrons, together with an ionization chamber, is lowered into the bore hole. The secondary gamma radiation, then emitted, is measured by means of the ionization chamber. The measurements yield information concerning the lithological characteristics of the surrounding material. The problem is somewhat different in moisture determination. Here it would appear that one should utilize two facts: first, hydrogen slows fast neutrons more effectively than any other common element; second, all hydrogen in most soils is, practically, in the form of water. Thus, a fast neutron source, an adjacent slow neutron detector, and a stop watch would appear to be basic items in a neutron method of soil moisture determination. The number of slowed up neutrons detected per unit time would be a measure of the moisture content.

THEORY

The possibilities of a neutron method for measuring soil moisture can better be understood by brief consideration of pertinent points in the theory.

Neutrons are uncharged subatomic particles the mass of which is almost the same as that of protons or of hydrogen nuclei. When neutrons interact with nuclei of atoms, the neutrons may be captured or scattered. If the neutrons are captured, unstable nuclei are usually formed. These nuclei either emit gamma rays or disintegrate with the emission of one or more light particles, usually a proton, an alpha particle, or two neutrons. If the neutrons are scattered, the process may be elastic or inelastic. If inelastic, the neutrons transfer enough of their kinetic energy to the nuclei to raise them to a higher energy state, from which they eventually return, emitting gamma rays. Elastic collisions are found to be much more probable than inelastic scattering, and also, for light elements, much more probable than capture.

In elastic collisions the laws of conservation of energy and momentum apply. The neutron simply gives up part of its kinetic energy—and in the form of kinetic energy—to the nucleus.

When a neutron collides elastically with a nucleus of mass number A , the average ratio ϵ of the energy E_2 of the neutron after the collision to that E_1 before, for all angles of scattering, is (11, p. 181)

$$\epsilon = \log_e \frac{E_2}{E_1} = 1 - \frac{A-1}{2A} - \log_e \frac{A+1}{A-1}. \quad (1)$$

The average energy E_n of a neutron after n collisions from an original energy state E_0 is

$$E_n = E_0 e^{-n\epsilon} \quad (2)$$

From equation (1) and known values of A , ϵ values were computed for the common soil elements (table 1). From these values and equation (2), the num-

their Technical Development Report 127, October 1950. It is important that the authors of the latter report, D. J. Belcher, T. R. Cuykendall, and H. S. Sack, of Cornell University, obtained substantially the same results as did the present authors. The Cornell equipment and soils tested were quite different from those reported here.

bers of collisions required to slow neutrons to thermal velocities when in hydrogen, silicon, or oxygen were further computed. The results are respectively 17, 240, and 136. Thus fourteen times as many collisions are required in silicon as in hydrogen; eight times as many in oxygen. In the latter calculations it was assumed that fast neutrons have energies E_0 of one million electron volts (1 mev) and that slowed neutrons have thermal energies E_n of one fortieth of an electron volt (1/40 ev).

Also of importance in the slowing of neutrons is the relative probability that a neutron will interact with an atom of a given element. This probability is expressed in the form of the nuclear cross section σ_s and is measured in barns, a barn being equivalent to 10^{-24} cm². This cross section depends primarily upon

TABLE 1
Values of ϵ and σ_s for principal soil elements*

ELEMENT	A	ϵ	σ_s	
			Fast neutrons	Thermal neutrons
			<i>barns</i>	<i>barns</i>
H	1	1.000	2.55	47.5
C	12	0.162	1.60	4.6
N	14	0.145	1.0	13.0
O	16	0.128	1.5	4.2
Cl	17	0.113	2.7	40.0
Ti	22	0.088	4.4	3.0
Na	23	0.086	2.6	3.6
Mg	24	0.082	2.0	3.5
Al	27	0.075	2.5	1.6
Si	28	0.071	3.2	2.5
P	31	0.063	3.0	4.0
S	32	0.061	2.6	1.3
K	39	0.050	3.8	3.0
Ca	40	0.049	4.9	1.5
Mn	55	0.037	3.0	12.0
Fe	56	0.036	13.0	3.0

* Values for σ_s are taken from Adair (1).

the energy of the neutron. It also depends, for the lightest elements and at low neutron velocities, upon chemical binding in the atom. The scattering cross section decreases as the neutron velocity increases, for energies below a few mev, for some of the lighter elements, including hydrogen.

Average values of the scattering cross sections for several elements are given in table 1. The cross sections for fast neutrons are for energies of about 2.5 mev and those for slow neutrons, 1/40 ev. The cross section for hydrogen increases greatly (47.5/2.55-fold) as the neutrons slow down; for most of the other elements in the soil, the cross section remains substantially the same.

Once the neutrons reach thermal energies they come to a thermal equilibrium with the surrounding atoms and no longer lose energy. They now scatter in accordance with the theories of gaseous diffusion until they are captured.

From a consideration of the energy reduction factors and scattering cross sections in table 1 it becomes clear why hydrogen should be more effective than other elements in slowing neutrons. Not only does a neutron lose more energy when it strikes a hydrogen nucleus (ϵ is large), but it also has a greater probability of striking such a nucleus (σ is large).

Mathematical formulation

The theory of neutron scattering may be formulated mathematically and the results utilized in the design of equipment for measuring soil moisture. The treatment outlined applies to the case of spherical symmetry.

Let $\rho(r)$ be the density of slow neutrons per unit volume in an element of volume distant r from a source of fast neutrons. Let t be the time and T the mean lifetime of a neutron. T is also the inverse of the probability of capture per unit time. Let D be the diffusion coefficient as ordinarily defined for a gas. Finally, let Q be the rate per unit volume at which thermal neutrons, that is, slow neutrons, are created.

Then from elementary transport theory (14), one can write the following equation of continuity

$$\partial\rho/\partial t = D\nabla^2\rho - (\rho/T) + Q \quad (3)$$

The term on the left is the time rate of variation of slow neutron density at the element of volume. The first term on the right (∇ is the Laplacian operator) represents the rate of increase of slow neutron density in the volume due to diffusion. The second term on the right represents the rate at which the slow neutrons disappear because of capture. The last term Q represents the rate at which slow neutrons are created by the slowing of fast ones.

Equilibrium is achieved almost immediately. Therefore in equation (3) $\partial\rho/\partial t$ may be set equal to zero.

It is now convenient to introduce the diffusion length L . This length is equal to one sixth the average distance from the point of origin to the point of capture of the thermal neutrons. The length includes not only the distance traveled during slowing but also the distance traveled before capture after being slowed. In terms of D and T , $L^2 = DT$.

Equation (3) may now be written

$$\nabla^2\rho - \rho/L^2 = -(T/L^2)Q \quad (4)$$

In equation (4) Q is usually calculated by means of the "age theory" (10). According to this theory Q satisfies the partial differential equation

$$\partial Q/\partial\theta = \nabla^2 Q + s\delta(\theta) \quad (5)$$

in which θ is the "symbolic age," s is a function depending on the shape of the source of the fast neutrons, and δ is the Dirac δ -function. Physically, θ has the dimensions of length squared. The Dirac δ -function is defined by: $\delta(r) = 0$ if $r \neq 0$; $\int \delta(r) dr = 1$ if the range of integration includes $r = 0$.

Solutions of equations (4) and (5) involve, of course, the boundary conditions and are difficult to obtain. The slowing down length and diffusion length are involved. The diffusion length has been defined. The slowing down length is defined as the average distance a neutron must travel in a medium before it is slowed to thermal velocity. The solution of interest here is that for a point source of fast neutrons in an infinite spherical medium. This solution has been presented by Wallace (14). It may be expressed in terms of the exponential function, $\exp x = e^x$ the error function, $\operatorname{erf} x = (2/\pi^{1/2}) \int_0^x e^{-y^2} dy$, and a quantity γ which is the ratio of the slowing down length to the diffusion length. Letting quantities A , B , C , and D , for abbreviation, be defined as below, Wallace finds the neutron

density $\rho(r)$ at a distance r from a point source of fast monoenergetic neutrons to be

$$\begin{aligned}\rho(r) &= [(\exp \gamma^2)(1 + \gamma^2)/(8\pi r)](AB - CD) \\ A &= \exp [-r(1 + \gamma^2)^{1/2}] \\ B &= 1 - \operatorname{erf} [\gamma - (r/2\gamma)(1 + \gamma^2)^{1/2}] \\ C &= \exp [r(1 + \gamma^2)^{1/2}] \\ D &= 1 - \operatorname{erf} [\gamma + (r/2\gamma)(1 + \gamma^2)^{1/2}]\end{aligned}\quad (6)$$

The significance of equation (6) may be brought out by plotting the density $\rho(r)$ of the slowed neutrons against distance r from the source, for several values of γ (fig. 1). Arbitrary units are used.

Here one sees that as γ approaches zero, the density of slowed neutrons is very large *near* the source $r = 0$; while if γ approaches infinity, the density of slowed neutrons will be small near the source. At great distances from the source, $\rho(r)$ is smaller for a small γ than for a larger γ . Also, at distances far from the

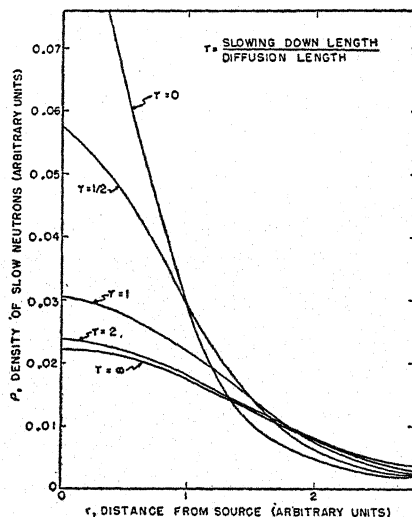


FIG. 1. SLOW NEUTRON DISTRIBUTION ABOUT A POINT SOURCE OF FAST NEUTRONS

source, percentage differences in $\rho(r)$ are small, regardless of how large are the differences in γ .

We are now ready to apply information gained from table 1. Obviously, because of the large ϵ and σ for hydrogen, the slowing down length for hydrogen will be very small compared to that of other common soil elements. That is to say, γ of figure 1 will be very small for hydrogen. Therefore, if a counter to detect slow neutrons is placed *near* a source of fast neutrons in soil, the percentage of counts registered will be a function largely of the amount of hydrogen³ (water)

³ Since γ is a ratio of two quantities, the slowing down length and the diffusion length, it is conceivable that these two quantities could vary in such a way that γ would stay constant with changing moisture content. The theory would then indicate that the neutron method would not work, at least for the spherical case. In designing our equipment, it seemed reasonable to assume that the diffusion length would remain *relatively* constant in soil when the moisture content changed. This conclusion seemed to be borne out by the experiments.

present in the soil. Other elements will have little effect. The counter, as stated, should be near the source. If the counter is placed far from the source, the counting rate, as the plot of equation (6) (fig. 1) shows, will be smaller for hydrogen than for other elements. In our soil moisture measuring experiment the neutron counter is placed as close as practical to the fast neutron source.

Soil hydrogen other than that in water

Most of the hydrogen found in the soil is contained in the soil water. A small amount is found in the mineral fraction, and this amount, being in chemical combination, should be relatively constant. Wetting or drying, as commonly understood, should not change the quantity of water in the mineral fraction.

The most important source of hydrogen in soil, other than that of soil water itself, is the hydrogen in soil organic matter. According to Waksman (13, p. 49), the hydrogen content of humus is about 5 per cent of its weight. As the amount of hydrogen in water is about 11 per cent of its weight, the amount of hydrogen in soil organic matter may be an appreciable part of the total hydrogen. But for practical agricultural work, one must remember that soils containing much organic matter also contain large amounts of water.

Feustel and Byers (4) have presented data on this point. They found the maximum moisture-holding capacity, the moisture equivalent, and the wilting percentage to be as follows: for a moss peat, 1057, 166, 82; for a sedge peat, 374, 112, 61; and for a reed peat, 289, 110 and 71. These values may be compared with those for a clay loam mineral soil, 44, 20, 7.

EXPERIMENTAL INVESTIGATION

Apparatus

The fast neutron source consisted of a mixture of polonium and beryllium (9) contained in a metal cylinder 17 mm. in diameter and 17 mm. in length. This emitted neutrons with a distribution of energies possessing a maximum at about 5.2 mev and had a half life of 140 days. At the time of the experiment, the source had a strength of about 10^4 neutrons per second. Only a few obvious precautions were necessary to eliminate danger to health.

A boron⁴ trifluoride slow neutron counter (7, p. 50) manufactured by Radiation Counter Laboratories, Chicago, Illinois, was used to measure the slow neutron density. This counter was cylindrical, with a diameter of 5 cm. and a length of 35.5 cm., and was filled to a pressure of 40 cm. of Hg. The counter was placed immediately on top of, and concentric with, the source of fast neutrons.

The counter was operated at 3,050 volts. This high voltage was derived from a high voltage power supply unit with a maximum output of 4,000 volts d.c. Since the power supply was unregulated, a Sorenson voltage stabilizer was used in the circuit to prevent damage to the counter. The stabilizer also prevented variations in counting rate due to possible extreme fluctuations in the line voltage

⁴ Boron is a soil constituent, but, as this element is present in only a few parts per hundred thousand in the soil (15), neutrons captured by soil boron will be negligible compared with those captured by the counter.

which fed the power supply. The pulses from the counter were fed through a Bell-Jordan linear amplifier (6) into a count recorder. The count recorder was a commercial scale-of-two scaler. In the course of the experiments one counter was accidentally broken. The data reported here are thus for two different counters. The accident provided a check on any counter effects.

Procedure

Five soils of varying texture and composition were selected for the experiment. These were Clarion silt loam, Monona silt loam, Wabash silt loam, O'Neil sand, and Putnam clay.⁵ The soils were placed in 4-gallon earthen crocks. Preliminary measurements showed that small samples were not satisfactory. The crocks were 25 cm. in diameter, 28 cm. deep, and were filled with soil to a depth of 22 cm. A hole 5 cm. in diameter and 18 cm. deep was drilled in the soil. The counter, with the neutron source fastened to its bottom, was lowered into the hole and supported in place.

The soils were saturated initially and the moisture contents lowered in steps by placing the sample in a sack in an oven at 105°C. for several hours. The soil was then mixed thoroughly and allowed to stand in the crock for several hours before a reading was taken. The counting rate of the slow neutron counter was determined at the various moisture contents. The moisture content per unit weight of oven-dry soil was measured by weighing and drying duplicate 100-gm. samples. These moisture samples were returned to the gross sample so that its size remained constant. The moisture content per unit volume of soil was also determined. This was done by dividing the weight of each 100-gm. oven-dry sample by the apparent volume of the same sample and then multiplying this quotient by the moisture content per unit weight.

The counting rate is, of course, a function of sample size. In an attempt to determine what size of sample was needed for effectively infinite size, the counter was waterproofed and placed in crocks of water of various diameters. The results would yield only a minimum value, for in partly dry soil the neutrons could travel much farther and still find a way back to the counter. The ratio of depth to diameter was 1.2 for all crocks. The end of the counter was placed to the same depth, 7 inches, in each water-filled crock.

The five soils were analyzed for organic carbon by igniting them in a carbon train (12). The percentages of hydrogen and total organic matter were calculated by using Waksman's (13) figures: 1 to 10 for the ratio hydrogen to carbon, and 2 to 1 for the ratio of total organic matter to carbon.

Results

The counting rate data were first calculated back to the first day of the experiment to correct for the exponential decay of the neutron source. The background count was found to be almost entirely a consequence of slow neutrons coming directly from the source. Therefore, this background rate, as it would be

⁵ Descriptions of the soils are given in "Principal Upland Soils of Iowa," Iowa Agr. Exp. Sta. Agron. 49 (Revised) [mimeographed].

constant except for the slow decay with time, was not subtracted from the total counting rate.

Figure 2 shows the counting rate versus moisture content per unit volume for the five soils studied. A single curve can be drawn to cover the whole moisture range from oven-dryness to saturation and for all five soils.

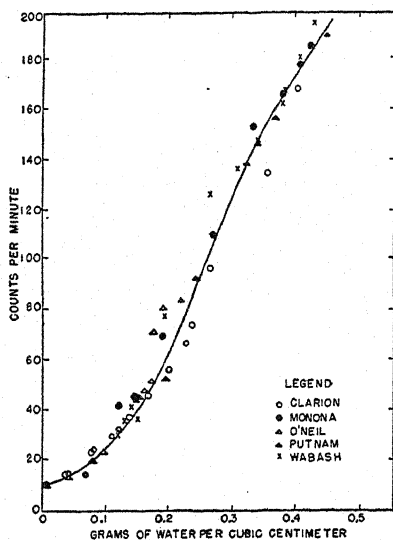


FIG. 2

FIG. 2. COUNTING RATE OF SLOW NEUTRONS AS A FUNCTION OF MOISTURE PERCENTAGE PER UNIT VOLUME FOR SEVERAL SOILS

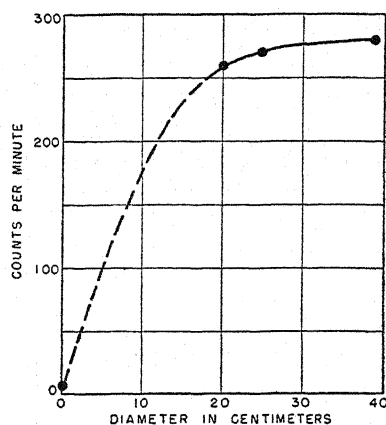


FIG. 3

FIG. 3. EFFECT OF SIZE OF SAMPLE ON COUNTING RATE WHEN SAMPLE IS WATER

TABLE 2

Density and organic matter content of five soils

SOIL	DENSITY	C	H	TOTAL ORGANIC MATTER
	<i>lb./cu. ft.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Clarion.....	73.5	1.1	0.11	2.2
Monona.....	63.5	1.8	0.18	3.6
O'Neil.....	94.4	0.24	0.02	0.5
Putnam.....	71.5	0.47	0.05	0.9
Wabash.....	62.2	3.3	0.33	6.6

Table 2 gives the density of each of the soils as well as the organic carbon content as found from the carbon train.

Figure 3 shows the curve obtained when the diameter of the water-containing crocks was varied. Increasing the diameter of the crock of water from 20 cm. to about 40 cm. increased the counting rate 8 per cent.

The point at diameter zero in figure 3 represents the counting rate of the source and counter taken in air. The broken line connecting the zero point with the rest of the curve is uncertain.

Other points of interest not shown in figure 3 are the following: Water more than 15 cm. below the bottom of the counter contributed very little to the total count. The wall thickness of the casks had negligible effect on the counting rate. Persons standing next to a cask had no perceptible effect on the counting rates, even though there is a large amount of hydrogen in the human body.

DISCUSSION OF RESULTS

It appears from figure 2 that a definite relationship exists between the soil moisture content and the counting rate of neutrons. Furthermore, the relationship between counting rate and soil moisture appears to be the same for the five soils—soils including a sand and a clay and varying in specific gravity from 62.2 to 94.4 pounds per cubic foot. The relationship is true, however, only if the moisture content is expressed in terms of a unit volume of soil. Different curves were obtained for each of the soils when moisture was expressed in terms of unit weight of oven-dried soil. In agricultural work, moisture on a volume basis is generally more desirable than on a weight basis.

Not all the experimental points fall closely on the curve of figure 2. Some of the deviations may be due to counting errors, and some to moisture sampling errors. The probable relative error \bar{e} in a set of n counts is given (8, p. 232) by $\bar{e} = 0.67n^{-1/2}$. To keep this error small, at least 1,000 counts were taken in most measurements. Thus the counting error will be less than about 2 per cent. Some of the scatter of the points in figure 2 is undoubtedly due to inaccuracies in moisture determinations. That uniform drying and mixing of the soil was not completely achieved was evidenced by differences between duplicate moisture samples. Some of the data in figure 2 were obtained with one counter; some with another. No discernible differences due to counters were detected.

Figure 2, as has been indicated, is of great interest because variations in soil texture and composition appear there to have negligible effect. To check this point further, the neutron source and counter were located first in air, away from soil, and then in oven-dry Clarion silt loam. The counting rate for air was 8.6 ± 0.2 counts per minute; for the loam it was 9.0 ± 0.3 counts per minute. Thus it appeared that the dry matter in soil contributed very little to the counting rate.

A method for determining soil moisture should be rapid. Figure 2 indicates that the present equipment does not yield rapid results at low moisture contents. At low moisture contents, about 100 minutes would be required to obtain the needed 1,000 counts. But the present apparatus was assembled because of availability and not necessarily because of desirability. In more suitable apparatus the neutron source might be strong (and more stable, so that correction for decay would not be required). In desirable apparatus a counting rate meter might be used instead of a counter with a watch.

It was beyond the scope of this experiment to study extensively the effect of size of soil sample on counting rate. Nevertheless from the few data obtained (fig. 3), one may conclude that water-saturated soil 1 foot away from the axis of the neutron source has a small but discernible effect on counting rate. In dry soil the effect would be larger. Figure 3 indicates also that the present ap-

paratus will not be suitable for small soil samples. Small samples would be suitable, according to the theory (see figure 1), if a smaller source and counter than the present ones were used. But in most instances a large sample size should be a distinct advantage. For small samples, a collimated source would be desirable. With a collimated source the moisture content in long narrow glass or metal soil tubes could be followed without disturbing the soil in the tube.

The depth of neutron source and counter in a soil auger hole will influence the counting rate, at least at depths comparable to the size of the source-counter unit. But it would seem that the unit would not have to be placed in an auger hole. With proper calibration, it would seem that a unit could be constructed for use at the soil surface. An investigator might then be able to walk over a field, reading simultaneously the water content of a certain depth of the surface soil directly. A portable counting rate meter would be required with the source-counter unit. There may be some difficulty in interpreting results. The matter seems worthy of investigation.

SUMMARY AND CONCLUSIONS

It has been shown theoretically, and experimentally for five soils, that a method involving the scattering and slowing of fast neutrons by hydrogen may be used for measuring soil moisture. The method rests primarily on two considerations: first, hydrogen is, practically, the only material that will slow fast neutrons; second, hydrogen in soils is present almost entirely in the form of water.

In applying the above concepts, a fast-neutron source and a slow-neutron counter (source and counter combined into a single unit) are lowered into a small auger hole in the soil. The counting rate of neutrons which have been slowed by soil hydrogen is a measure of the moisture content.

Based on the theory and the tests, the following conclusions are drawn.

The method appears valid from oven-dryness to water-saturation.

The method yields the moisture content per unit volume directly—not moisture content per unit oven-dry weight.

The method requires but a single calibration for all mineral soils (but the calibration depends on the depth of sample and other geometrical factors).

The method appears to be independent of soil temperature, texture, composition, compaction, and concentration of soil solution.

The method should be particularly useful in measuring soil moisture in the field *in situ*.

The foregoing statements apply to mineral soils. Soils high in humus content, as mucks, present a special problem. The method should be adaptable to organic soils, however, if the hydrogen content in the organic matter when dry is constant.

Design of a portable apparatus, suitable for field measurements, awaits development. The possibility of constructing portable equipment for measuring the amount of water in a certain depth of the surface soil is suggested. With the envisioned equipment it would not be necessary to disturb the soil in any way. The moisture detection unit could be held at, or just above, the surface of the soil.

REFERENCES

- (1) ADAIR, R. K. 1950 Neutron cross sections of the elements. *Rev. Mod. Phys.* 22: 249-289.
- (2) CORK, J. 1947 Radioactivity and Nuclear Physics. D. van Nostrand Co., New York.
- (3) FEARON, R. E. 1949 Neutron well logging. *Nucleonics*. 4(6): 30-42.
- (4) FEUSTEL, I. C., AND BYERS, H. G. 1936 Comparative moisture-absorbing and moisture-retaining capacities of peat and soil mixtures. U. S. Dept. Agr. Tech. Bul. 532.
- (5) GERDEL, R. W., HANSEN, B. L., AND CASSIDY, W. C. 1950 Use of radioisotopes for the measurement of water equivalent of a snow pack. *Trans. Amer. Geophys. Union* 31: 449-453.
- (6) JORDAN, W. H., AND BELL, P. R. 1947 A general purpose linear amplifier. *Rev. Sci. Inst.* 18: 703-708.
- (7) KORFF, S. A. 1946 Electron and Neutron Counters. D. van Nostrand Co., New York.
- (8) LAPP, R. E., AND ANDREWS, H. L. 1948 Nuclear Radiation Physics. Prentice-Hall, Inc., New York.
- (9) MCCALLUM, K. J. 1949 Preparation and use of neutron sources. *Nucleonics* 5(1): 11-21.
- (10) MARSHAK, R. E. 1947 Theory of the slowing down of neutrons by elastic collision with atomic nuclei. *Rev. Mod. Phys.* 19: 185-238.
- (11) OREAR, J., ROSENFELD, A. H., AND SCHLUTER, R. A. (Compilers). 1949 Nuclear physics notes from a course by Enrico Fermi. University of Chicago Press, Chicago.
- (12) SLATER, R. M. 1916 A rapid method for the accurate determination of total carbon in soils. *Indus. and Engin. Chem.* 8: 637-639.
- (13) WAKSMAN, S. A. 1938 Humus, ed. 2, p. 49. Williams & Wilkins Co., Baltimore.
- (14) WALLACE, P. R. 1949 Neutron distributions in elementary diffusion theory: I. *Nucleonics*. 4(2): 30-55.
- (15) WHETSTONE, R. R., ROBINSON, W. O., AND BYERS, H. G. 1942 Boron distribution in soils and related data. U. S. Dept. Agr. Tech. Bul. 797.

IONIZATION OF SOILS AND SOIL COLLOIDS: III. POTASSIUM-CALCIUM RELATIONSHIPS IN ILLITE, KAOLINITE, AND HALLOYSITE

S. A. BARBER AND C. E. MARSHALL

Missouri Agricultural Experiment Station¹

Received for publication May 28, 1951

The experimental procedures followed in this study were described in Parts I and II of the series (1, 8). The use of mean free bonding energies alongside activities and fractions active in the evaluation of the results has been continued along the lines developed in Part II. The cationic activities given are calculated from the mean of four measured potentials, two in each of duplicate clay systems.

MATERIALS USED

Illite

Two samples of illite were used. One was from the Illinois Clay Products Company and is known commercially as Grundite. Our electrochemical work with illite has been chiefly concentrated on this material. A mineralogical description has been given by Grim and Bradley (5). The fraction used was $<1 \mu$, since very fine material was present only in small quantity.

The second sample was from Maquoketa shale, obtained from the Bureau of Plant Industry and originating also in Illinois. Mineralogical and chemical studies have been published by Grim, Bray, and Bradley (4). The fraction used was $<2 \mu$.

The illites are somewhat hydrated micas containing less K than does muscovite. The charge on the Si layers is high. Probably the ionization occurs chiefly on the Si layers exposed as outer surfaces. The weathering of potash micas on the outer surfaces probably involves a replacement by H^+ , Ca^{++} , Na^+ , or Mg^{++} of some of the K^+ that balances the lattice charge, since these are found as exchange cations in colloidal illites.

Kaolinite

The same sample of kaolinite as in previous studies was used (3, 9, 10, 11). It is from Langley, South Carolina, and appears to be comparatively pure. The fraction $<2 \mu$ was used throughout, since very little fine colloidal material was present. Ionization in kaolinite clays is usually supposed to occur primarily at crystal edges, although flat external surfaces perhaps also play a part. The lattice itself is uncharged.

Halloysite

This halloysite of commercial origin was labeled "Kamee" kaolin and has been used by Mehlich and Colwell at North Carolina (14). Electron microscope

¹ Contribution from the department of soils, Missouri Agricultural Experiment Station Journal Series 1255. The senior author is now at Purdue University.

observations indicated that it consisted chiefly of halloysite (long rods) with some admixture of kaolinite (probably not more than 10 per cent). A montmorillonite group clay is probably also present, since the sample gave a light blue coloration on treatment with benzidine sulfate. X-ray examination also indicated the presence of a montmorillonite group clay in small amount. From the work of Bates, Hildebrand, and Swineford (2) it is now established that the rod-shaped particles seen in electron micrographs of halloysite and endellite are hollow tubes, with internal diameters varying from 20 to 100 m μ . The surface chemistry of halloysite is little known except by analogy with that of kaolinite. The hydrated form has been renamed "endellite." Structural interpretations of x-ray results indicate that kaolinite layers alternate with layers of water molecules in hexagonal packing, thus giving rise to material of composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$.

GENERAL ELECTROCHEMISTRY OF CLAYS STUDIED

Illite

Previous investigations have given a detailed picture of the ionization of Grundite illite when single metallic cations are present. Titration curves obtained by treating the H clay with KOH (9), NaOH (11), NH_4OH (10), $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$ (3), have been published. Evidently, monovalent ions are less ionized from illite than from montmorillonite and kaolinite. The divalent ions form with illite a series in which Mg and Ca give higher active fractions than for montmorillonite and kaolinite, whereas Ba is conspicuous for its low active fraction. The Ba ion, it will be recalled, is almost identical with K^+ in size, and was shown by Page and Baver (15) to enter a beidellite clay with considerable fixation upon drying.

Comparison of illite with montmorillonite, beidellite, and kaolinite, led to the conclusion that illite with monovalent cations was clearly the least ionized of the four clays. Yet with divalent cations it was the highest in ionization throughout, except that kaolinite gave a higher value with Ba^{++} (3). The interactions of monovalent and divalent cations should thus prove extremely interesting.

Kaolinite

With monovalent cations, kaolinite was consistently the most highly ionized of the four minerals studied (9); with divalent cations, it varied in its relative position according to the cation concerned and the degree of saturation (3). Comparisons are somewhat complicated by the fact that the inflection point on the pH curves corresponds to a lower equivalence for divalent than for monovalent cations. The titration curves of kaolinite with $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$ show consistently that the order of ionization is $\text{Ba}^{++} > \text{Ca}^{++} > \text{Mg}^{++}$, whereas the other clays give differing orders at different degrees of saturation. The fact that Mg is less ionized than Ca may well be reflected in uptake by plants. This has clearly been demonstrated by Mehlich and Colwell for the kaolinitic Durham soil (13).

The numerous points of difference between kaolinite and the montmorillonite

and micaceous clays may be explained by the differing mechanisms of ionization. Kaolinite has planar Si_2O_3 surfaces which are much more nearly electrically neutral than those of clays of the 2:1 type. It also has planes of OH-groups like gibbsite. Strong mechanisms for ionization would be found only at the terminal edges.

Halloysite

Nothing has previously been published on the general electrochemistry of halloysite. Strong mechanisms for ionization would be expected to operate at edges only, as in kaolinite. The specific surface might be expected to be somewhat greater than in kaolinite, because the strain caused by the imperfectly fitting layers of water molecules would, according to Bates *et al.* (2), cause relatively thin packets of plates to curl, giving hollow tubes.

RESULTS

Illite

Illite from "Grundite." The titration curve data for K and Ca and the data for the mixed systems at equivalence (28.5 me. per 100 gm.) are given in figures 1 and 2. Figure 1 illustrates graphically how H and Ca affect the K-ion activity, the fraction active, and the mean free bonding energy of the potassium ion as various proportions of K are present. Figure 2 gives similar data for Ca as it is affected by H or K.

A comparison of the titration curve with $\text{Ca}(\text{OH})_2$ and that given by Chatterjee and Marshall (3) in a comparison of Mg, Ca, and Ba, indicates that the present series gives distinctly lower fractions active for Ca. This may be due to a small amount of organic impurity in the clay examined by Chatterjee and Marshall. This would partly explain the wide discrepancy found between Mg and Ca on the one hand and Ba on the other, with respect to their ionization from illite. The general conclusions that Ba ionizes less than do Mg and Ca is not affected. It is evident that such low activities as are found with divalent systems may be strongly affected by electrolyte impurities down to 10^{-5} molar, the errors being appreciable chiefly at early points on the titration curves.

The most noteworthy feature of the K curves is their distinct resemblance to those of Putnam clay and attapulgit reported in Part II of this series. Small amounts of K are held with high bonding energies in the presence of Ca.

The Ca curves also resemble those of Putnam clay, with a change in the relative position of the Ca-K and Ca-H curves at about 50 per cent saturation. About this value the Ca-K systems give slightly higher Ca activities than do the Ca-H systems. Below 50 per cent saturation the situation is reversed, but the Ca activity is here so low that few measurements were possible.

Illite from Maquoketa shale. The equivalence (22 me. per 100 gm.) was somewhat lower than that of the Grundite illite. In general electrochemical behavior, the two clays proved to be very similar. Figures 3 and 4 demonstrate this. Thus the Maquoketa illite showed in the K-Ca curves that small amounts of K are held with much greater bonding energy than larger quantities. The crossing

over of the Ca curves for the Ca-K and Ca-H systems occurred at about 70 per cent saturation, somewhat higher than for the Grundite sample. One quantitative difference was noted. The Maquoketa sample gave a distinctly lower bonding energy toward Ca than the Grundite, although with K alone they were almost identical.

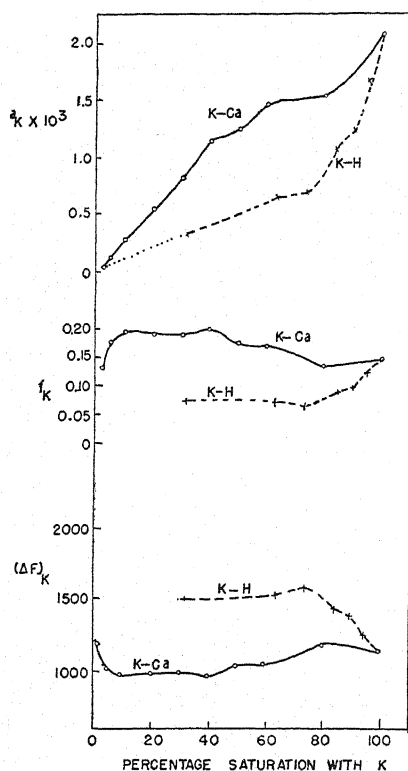


FIG. 1

Fig. 1. POTASSIUM-ION ACTIVITIES (UPPER CURVES), FRACTIONS ACTIVE (MIDDLE CURVES), AND MEAN FREE-BONDING ENERGIES (LOWER CURVES) FOR 5 PER CENT GRUNDITE ILLITE IN K-Ca AND K-H SYSTEMS

100 per cent saturation = 28.5 me./100 gm.

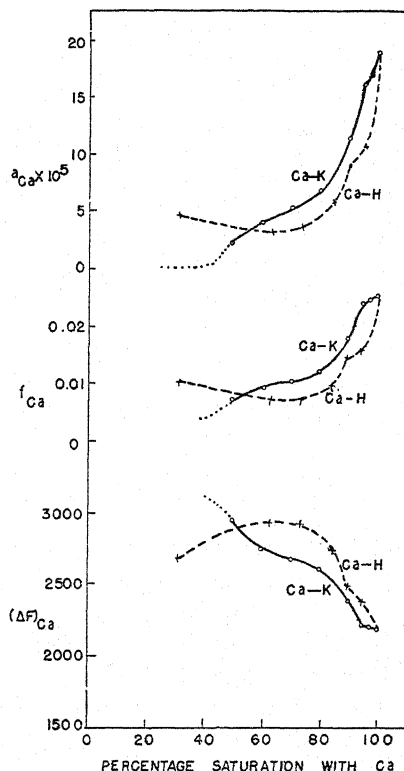


FIG. 2

FIG. 2. CALCIUM-ION ACTIVITIES (UPPER CURVES), FRACTIONS ACTIVE (MIDDLE CURVES), AND MEAN FREE BONDING ENERGIES (LOWER CURVES) FOR 5 PER CENT GRUNDITE ILLITE IN Ca-K AND Ca-H SYSTEMS

100 per cent saturation = 28.5 me./100 gm.

General discussion. The fact that in general electrochemical behavior, the illite clays show many resemblances to Putnam clay, which is a beidellite, need occasion no surprise. Both types are characterized by a predominant negative charge on the Si layers. Beidellite-like clays probably can be formed under natural weathering conditions from micaceous clays, but other processes seem to be involved besides the replacement of the K^+ by other cations and the

change from a rigid to an expanding lattice. The exchange capacities of those beidellites which are K-free are not high enough to correspond to all the K positions in the illites. These positions, in a sample with only 5 per cent K would be equivalent to 128 me. per 100 gm., whereas the highest exchange capacity recorded for a beidellite is 100 me. and for our Putnam clay 70 me.

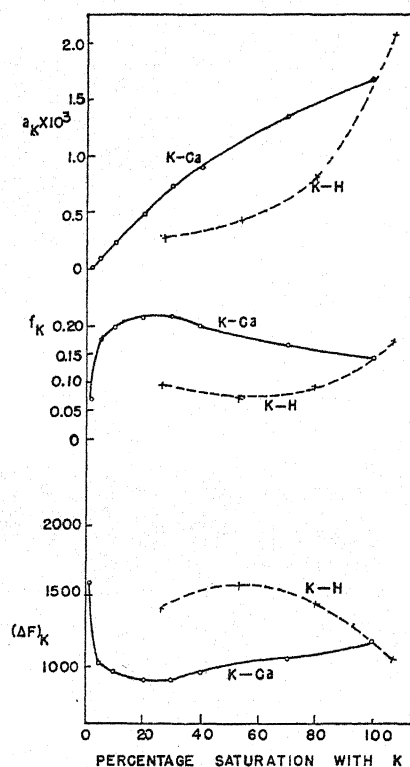


FIG. 3

FIG. 3. POTASSIUM-ION ACTIVITIES (UPPER CURVES), FRACTIONS ACTIVE (MIDDLE CURVES), AND MEAN FREE BONDING ENERGIES (LOWER CURVES) FOR 5 PER CENT MAQUOKETA ILLITE IN K-Ca AND K-H SYSTEMS

100 per cent saturation = 22.5 me./100 gm

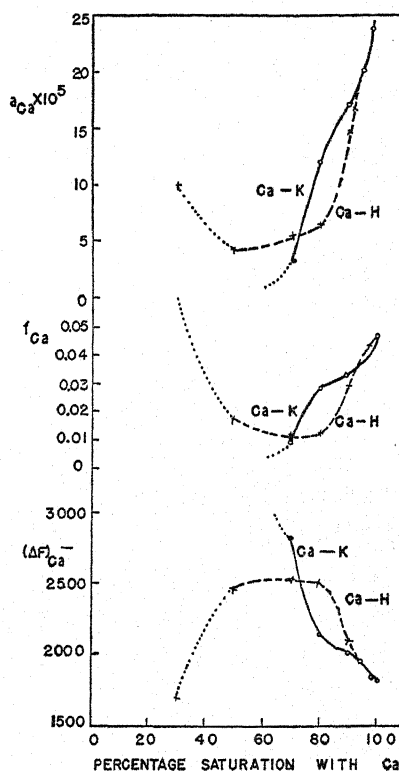


FIG. 4

FIG. 4. CALCIUM-ION ACTIVITIES (UPPER CURVES), FRACTIONS ACTIVE (MIDDLE CURVES), AND MEAN FREE BONDING ENERGIES (LOWER CURVES) FOR 5 PER CENT MAQUOKETA ILLITE IN Ca-K AND Ca-H SYSTEMS

100 per cent saturation = 22.5 me./100 gm.

A feature which distinguishes these illites from beidellite and other members of the montmorillonite group is the ionization of Ca relative to K. Calculated per equivalent, the bonding energies for K and Ca are closely similar in Wyoming bentonite and Putnam clay. For the two illites studied, the bonding energy per equivalent of Ca is appreciably below that of K. This evidently reflects in some measure the tendency toward potash fixation in the illites. When illite clays are

compared with beidellites at the same total concentration of Ca and the same degree of saturation, this means that the Ca activity of the illite clay would be greater than that of the beidellite by a factor of 2 to 3. This relationship holds for both the Ca-K and the Ca-H systems. This puts the soils dominated by illite minerals in a much more favorable position, as regards the Ca nutrition of plants, than soils dominantly beidellitic.

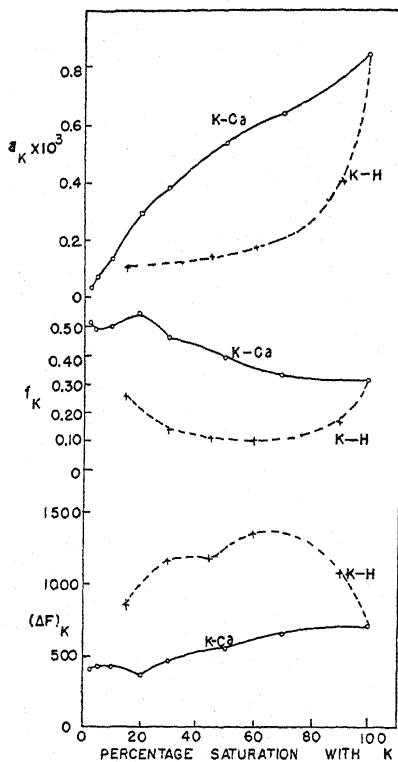


FIG. 5

FIG. 5. POTASSIUM-ION ACTIVITIES (UPPER CURVES), FRACTIONS ACTIVE (MIDDLE CURVES), AND MEAN FREE BONDING ENERGIES (LOWER CURVES) FOR 10 PER CENT KAOLINITE IN K-Ca AND K-H SYSTEMS

100 per cent saturation = 2.75 me./100 gm.

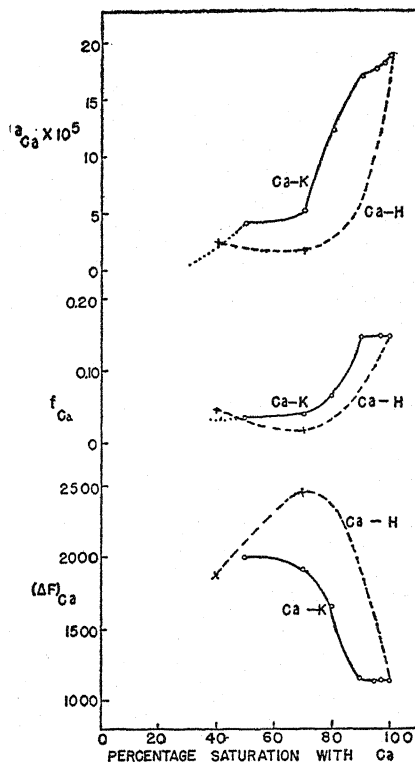


FIG. 6

FIG. 6. CALCIUM-ION ACTIVITIES (UPPER CURVES), FRACTIONS ACTIVE (MIDDLE CURVES) AND MEAN FREE BONDING ENERGIES (LOWER CURVES) FOR 10 PER CENT KAOLINITE IN Ca-K AND Ca-H SYSTEMS

100 per cent saturation = 2.75 me./100 gm.

Kaolinite

Experimental. The equivalence of kaolinite was taken as 2.75 me. per 100 gm., close to the inflection on the pH curve for KOH. As pointed out by Chatterjee and Marshall (3), the inflection with $\text{Ca}(\text{OH})_2$ lies at a somewhat lower value. The clay concentration used was 10 per cent throughout. Figures 5 and 6 present the results.

The individual titration curves with K and Ca differ in some details from those previously published. As regards K, the active fractions reported here for the lower degrees of saturation lie somewhat below those published in 1941 by Marshall and Bergman (10), although at saturation they agree very closely. In the Ca titration curves, the present series give values measurably higher than those reported by Chatterjee and Marshall (3). These variations may be due to variations in the efficiency with which traces of impurities were removed from the different batches of clay. The source material was the same throughout. Although the absolute positions of the different curves may thus be somewhat uncertain, the general conclusions drawn from a comparison of the K-H, Ca-H, and K-Ca curves will scarcely be affected, since these were all carried through on the same batch of clay.

The K-activity determinations and the quantities derived from them clearly show that K-Ca systems give higher K-ion activities than do K-H systems. The active fraction of K in the K-Ca systems was relatively constant at about 0.5 between 0 and 25 per cent saturation with K. Between 25 and 100 per cent saturation with K, it fell slowly to 0.3. This suggests two fairly distinct groups of K atoms.

The corresponding Ca activity determinations could be carried out only between 50 and 100 per cent Ca on the Ca-K systems, but the results show that below 50 per cent Ca the active fraction of Ca in the Ca-K systems would be below that in the Ca-H systems. Between 50 and 100 per cent Ca, the reverse is true. In this region the Ca activity is enhanced by the presence of K.

General discussion. The comparison of kaolinite with illite and with beidellite is likely to be of special importance in clarifying the differing responses to liming and fertilizer practices of northern and southern soils. Comparisons are rendered somewhat difficult by the differing exchange capacities of these clays, because, strictly, they can be made only at the same total cation concentrations. With single monovalent cations, kaolinite was found to be distinctly more highly ionized than beidellite and illite at all degrees of saturation. With single divalent cations, kaolinite was most highly ionized at pH values over 6, but below pH 6 the ionization would place this clay between illite and beidellite. When the mixed K-Ca systems at full saturation are considered, the curve connecting the activity ratio a_K/a_{Ca} with degree of K saturation lies considerably to the right of and below the corresponding curves for beidellite and illite. This is largely a consequence of the high ionization of the monovalent cation, following the rule discussed in Part II of this series. It may be said, therefore, that near neutrality a kaolinite clay will show a very distinctly lower a_K/a_{Ca} ratio than any of the other clays examined, when comparisons are made at the same proportions of exchangeable K and Ca, and the same total concentration of cations.

Halloysite

As has been noted, the halloysite contained some kaolinite and also sufficient of a montmorillonite, beidellite, or mixed layer clay to give a clear blue color with benzidine sulfate. The results, therefore, are not given in detail, but certain conclusions can be drawn by a comparison of the results but those for kaolinite.

The pH titration curves with KOH and $\text{Ca}(\text{OH})_2$ each showed a single inflection at about 7 me. per 100 gm. The fraction active for K was below that for kaolinite throughout the whole course of the titration curve. At the equivalence point, kaolinite gave a value of about 0.3, whereas halloysite gave 0.14. In the Ca series the disparity was marked; at equivalence the active fraction was 0.15 for kaolinite but only 0.016 for halloysite. These differences at equivalence could not be due wholly to the presence of a montmorillonite impurity, although this might have a considerable effect at early points on the titration curves.

The mixed K-Ca systems at equivalence showed interesting features. For very small proportions of exchangeable K (2 per cent or less) the active fraction was small, corresponding to a high bonding energy. From 5 per cent K onward, the active fraction was high, although not so high as for kaolinite, and the relationships of the K-H and K-Ca curves were about the same as those for kaolinite. These results suggest the presence of a beidellite or illite type of impurity. Such clays are characterized by a high bonding energy for small proportions of potassium and a rapid falling off between 2 and 5 per cent exchangeable K.

The Ca activities measured in the mixed Ca-K systems were very markedly below those for kaolinite, as they were in the Ca-H systems. The general relationships of the activities and fractions active for the Ca-H and Ca-K systems were comparable with those of kaolinite. Above 60 per cent exchangeable Ca, the Ca activity was appreciably higher in the Ca-K system than in the Ca-H system. It seems likely that with smaller proportions of Ca the curves would cross, but it was not possible to establish this, since the Ca activities were so exceedingly small.

Obviously, further work on the electrochemistry of halloysite, both hydrated (endellite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$) and dehydrated ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), with samples of established purity should prove of great interest.

POTASSIUM-CALCIUM RATIOS

As in Part II of this series, interesting information can be derived by plotting the activity ratio a_K/a_{Ca} against the cationic percentage (by equivalents) on the exchanger. It was pointed out that in absence of disturbing factors, the rule connecting active fraction and cationic valency has as its corollary the deduction that clays having a low fraction active with monovalent cations should give high values of a_K/a_{Ca} and *vice versa*. Thus the order of the curves for different clays, so plotted, should be predictable. A major disturbing factor is that each cation on each clay is characterized by a wide distribution of bonding energies rather than by a single value. This shows itself very strongly when two cations are present simultaneously on a given clay. Its effect can be gauged by a graphical comparison of a_K/a_{Ca} for homionic and mixed systems (fig. 7). The homionic systems give values for a_K/a_{Ca} (each at equivalence), which fall in the order predicted from the f_K values. (Maquoketa illite is the only exception.) When the a_K/a_{Ca} curves are drawn for the mixed systems, the curve for Wyoming

bentonite lies above those for Putnam clay and for illite, whereas according to the aforementioned rule it should lie below them. This may be regarded as a lowering of the a_K/a_{Ca} values for beidellites and illites due to the tendency of K to become fixed. The Maquoketa illite curve is even further displaced in this direction.

ORDER OF ADDITION IN ITS EFFECT ON ACTIVITIES

In certain systems (H-Ca permutites) evidence obtained in Wiegner's laboratory from cation-exchange experiments indicated that the order of addition

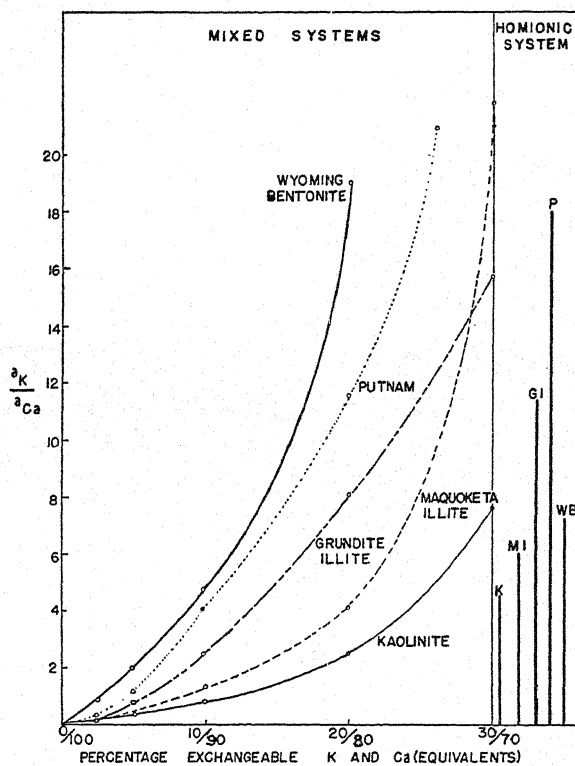


FIG. 7. ACTIVITY RATIOS a_K/a_{Ca} FOR HOMIONIC AND FOR MIXED K-Ca CLAYS

influenced subsequent replacement. It is naturally of considerable importance to determine whether this holds true for the activities measured in mixed clay systems. Calcium-potassium clays were therefore investigated, both cationic activities being measured. In each case two systems of the same composition were compared. In one, the $Ca(OH)_2$ was added first, the system allowed to stand for 7 days, then the KOH was added. Activity measurements were made 2 days after this second addition. In the second, the order of the additions was reversed, the other factors remaining the same. Four clay systems were set up: 2.5 per cent Putnam clay, 5 per cent Maquoketa illite, 1.5 per cent attapulgite,

and 10 per cent halloysite. In the first three, the saturations with Ca and K were respectively 95 per cent and 5 per cent; in the last (halloysite) they were 80 per cent and 20 per cent. These proportions were chosen so as to give reasonably accurate activity determinations for the Ca.

When the respective systems were compared, no significant differences were found. Even attapulgite, with its channels of fixed cross section, were completely reversible. It may therefore be concluded that clays come to equilibrium fairly readily. Neither the fact that different cations show different bonding energies nor the existence of a broad range of bonding energies for a given cation on a given clay causes a lack of reversibility or a dependence on previous history, so far as the activities of Ca and K are concerned.

COMPARISON WITH PREVIOUS SERIES

The results for single cation activities in this and the previous paper are in part repetitions of K and Ca determinations reported in earlier publications. Mention has already been made of the possibility of error by contamination by soluble electrolytes and of its serious consequences where the active fraction is low. Where two series are available on the same batch of clay, the one giving the lower active fraction is obviously the more likely to be accurate. The present K series with Putnam clay gives appreciably lower active fractions than those reported by Marshall and Bergman in 1942 (9). Sodium determinations by Marshall and Krinbill (11) gave lower fractions active than in the 1942 K series. It thus appeared, particularly in the Putnam clay, as if the order of ionization were $K > Na$, whereas one would naturally expect $Na > K$. This matter has been re-examined by McLean (7) in a study of Na and K activities in Putnam clay. The order of extent of ionization is now established as $Na > K$, and the K values found were in good agreement with the present series. The 1942 series for potassium was therefore most probably affected by electrolyte impurity.

For divalent cations also, some discrepancies in different series have already been commented upon. The preliminary results on kaolinite reviewed in 1948 (12) gave much higher fractions active for early parts of the titration curve than were found in the series reported by Chatterjee and Marshall (3). Calcium, like Mg and Ba, is now found to give low fractions active up to 70 per cent saturation with base. Kaolinite thus resembles the other clays, as regards the general course of the titration curves, but differs from them in the order of ionization, which is very consistently $Ba > Ca > Mg$.

SUMMARY

The potassium-calcium relationships of two illites (Grundite and Maquoketa) were found by activity measurements to be closely similar to those of Putnam clay (beidellite) in general features. Increase in calcium saturation greatly increased the potassium activity. Potassium lowered the calcium activity up to about 60 per cent saturation and beyond this point increased it slightly. Compared with montmorillonite group clays, illites tend to hold potassium more tenaciously but calcium less tenaciously.

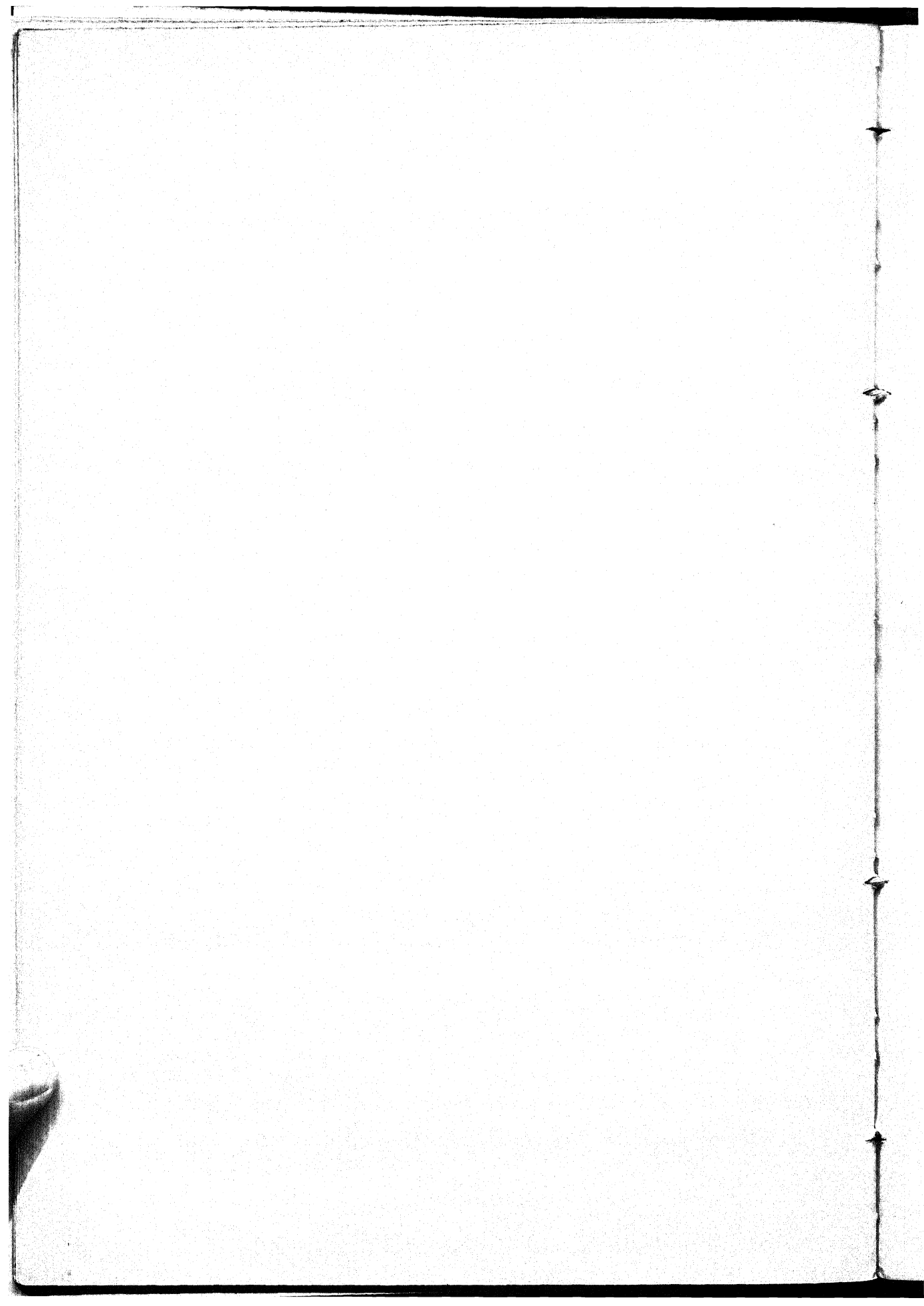
The potassium-calcium relationships of kaolinite show qualitative similarities to those of beidellite and the illites, but quantitatively they are distinctly different. Calcium increased the potassium activity (as was found for all the clays examined), and potassium decreased the calcium activity below 60 per cent saturated but increased it slightly beyond this point. The a_K/a_{Ca} ratio of kaolinite was much lower than that of the other clays, because of the relatively high ionization of both cations near saturation.

The results with halloysite were probably affected by kaolinite and a montmorillonite group clay as impurities. In general, they were similar to those of kaolinite, but with distinctly lower active fractions.

With Putnam clay, Maquoketa illite, attapulgite, and halloysite, it was found that the order of addition of base to the acid clay made no difference to the calcium and potassium activities measured in the mixed systems.

REFERENCES

- (1) BARBER, S. A., AND MARSHALL, C. E. 1951 Ionization of soils and soil colloids: II. *Soil Sci.* 72: 373-385.
- (2) BATES, T. E., HILDEBRAND, F. A., AND SWINEFORD, A. 1950 Morphology and structure of endellite and halloysite. *Amer. Mineral.* 35: 463-484.
- (3) CHATTERJEE, B., AND MARSHALL, C. E. 1950 Studies in the ionization of magnesium, calcium, and barium clays. *Jour. Phys. Colloid Chem.* 54: 671-681.
- (4) GRIM, R. E., BRAY, R. H., AND BRADLEY, W. F. 1937 The mica in argillaceous sediments. *Amer. Mineral.* 22: 813-829.
- (5) GRIM, R. E., AND BRADLEY, W. F. 1939 A unique clay from the Goose Lake, Illinois area. *Jour. Amer. Ceramic Soc.* 22: 157-164.
- (6) MCLEAN, E. O., AND MARSHALL, C. E. 1949 Reciprocal effects of calcium and potassium as shown by their cationic activities in montmorillonite. *Soil Sci. Soc. Amer. Proc.* (1948) 13: 179-182.
- (7) MCLEAN, E. O. 1951 Interrelationships of potassium, sodium, and calcium activities in a beidellite clay. *Soil Sci. Soc. Amer. Proc.* (1950) 15: 102-106.
- (8) MCLEAN, E. O., BARBER, S. A., AND MARSHALL, C. E. 1951 Ionization of soils and soil colloids: I. *Soil Sci.* 72: 315-325.
- (9) MARSHALL, C. E., AND BERGMAN, E. W. 1942 Electrochemical properties of mineral membranes: II. *Jour. Phys. Chem.* 46: 52-61.
- (10) MARSHALL, C. E., AND BERGMAN, W. E. 1942 Electrochemical properties of mineral membranes: IV. *Jour. Phys. Chem.* 46: 327-334.
- (11) MARSHALL, C. E., AND KRINBILL, C. A. 1942 Clays as colloidal electrolytes. *Jour. Phys. Chem.* 46: 1077-1090.
- (12) MARSHALL, C. E. 1948 Ionization of calcium from soil colloids and its bearing on soil-plant relationships. *Soil Sci.* 65: 57-68.
- (13) MEHLICH, A., AND COLWELL, W. E. 1944 Influence of nature of soil colloids and degree of base saturation on growth and nutrient uptake by cotton and soybeans. *Soil Sci. Soc. Amer. Proc.* (1943) 8: 179-184.
- (14) MEHLICH, A., AND COLWELL, W. E. 1946 Absorption of calcium from kaolin and bentonite at varying levels of calcium. *Soil Sci.* 61: 369-374.
- (15) PAGE, J. B., AND BAVER, L. D. 1940 Ionic size in relation to fixation of cations by colloidal clay. *Soil Sci. Soc. Amer. Proc.* (1939) 4: 150-155.



BOOKS

African Soils. Volume 1, number 1. Inter-African Information Bureau for Soil Conservation and Land Utilization. 57 Rue Cuvier, Paris V, October, 1951. Pp. 112. Yearly subscription, 1,600 francs.

This is a quarterly review. The first issue contains four papers on conservation in British Colonial Africa, Intertropical Zone of the French Union, Union of South Africa, and Belgian Congo, by Greene, Guillaume, Adler, and Jurion, respectively. It also contains the Inter-African organizations for soil conservation, a review of the Fourth International Congress of Soil Science, abstracts on climatology and ecology, and bibliography of publications received and list of periodicals issued by the Permanent Soils Bureau, the sponsor of the journal. The first number contains much interesting material, which is attractively presented in both English and French.

Contribution à l'Étude de la Symbiose Bactérienne chez les Legumineuses. By ALBERT DEMOLON. *Revue Générale de Botanique*. Librairie Generale de L'Enseignement, Paris, 1952. Pp. 126, plates 12, figs. 20. Paper-bound.

This is a separate from Volume 58 of "*La Revue Générale de Botanique*." It is a report of the author's personal work with *Bacterium radicicola* (Rhizobium), together with a review of some of the more important recent research on this organism and its functioning. Following a short history of the early work of Hellriegel, Wilfarth, Schloesing, and Laurent, the author considers the characteristics of Rhizobium and of its phage, the nature of the root-infecting process, the development and nature of the nodules, the fixation process, and some practical applications. He gives a very interesting presentation of the subject. The table showing the characteristics of the nodules of the several groups of legumes and the plates of microphotographs of the bacteria merit special mention.

The Desert Year. By JOSEPH WOOD KRUTCH. William Sloane Associates, New York, 1952. Pp. 270. Price \$3.75.

This is the story of a whimsical, observing college professor who, on sabbatical leave for 15 months, explored and fell in love with a desert. He is intrigued by flowers that carpet wide expanses at propitious periods; cacti and the living things that are closely associated with them; disastrous floods that run rampant after freak storms; cattle that are known to be around but are seldom seen; frogs that suddenly appear and reproduce after a rain and then disappear to await the next rain, possibly a year later; and bats that, at some unknown signal, emerge from their caves in regular order a few seconds apart and disappear over the horizon in a counterclockwise spiral. The net effect of the book is to make the reader want to pick out a desert of his own for leisurely observation of the life that abounds in it.

✓ *The Design and Analysis of Experiments*. By OSCAR KEMPTHORNE. John Wiley and Sons, Inc., New York, 1952. Pp. 631. Price \$8.50.

This book is intended not only for the experimenter but for the mathematician

who is concerned with the validity of statistical concepts as applied to agricultural experimentation. The author, a student of Yates, is now at Iowa State College, where he teaches courses in the design of experiments. After a general introduction to statistics, he proceeds with a consideration of the mathematical bases and then deals with randomization, Latin squares, plot techniques, factorial designs, split-plot experiments, fractional replication, lattices, and block designs. The book should be of special interest to instructors in this field of study.

The Enzymes, Chemistry and Mechanism of Action. Volume 2, part 2. Edited by JAMES B. SUMNER AND KARL MYRBÄCK. Academic Press, Inc., New York, 1952. Pp. 791-1440. Price \$14.

This is the last of the four units into which these two encyclopedic volumes are divided. The 17 contributors include Augustinsson from Sweden, Breusch from Turkey, Krebs and Elsdon from England, and Rautanen and Virtanen from Finland, all the other authors being from the United States. The 14 chapters, 65 to 78 inclusive, deal with bacterial fermentation, enzymes in detoxication, synthesis of urea, peptide bonds, glutamine, and acetylcholine, oxidative assimilation by microorganisms, carbon dioxide fixation, carbohydrate-fat conversion, bacterial and green-plant photosynthesis, nitrogen assimilation, tumor enzymology, and enzyme technology. The index, covering the entire second volume, includes the work of some 3,750 authors. The contents of this fourth unit live up to the high standards set for the entire set. The authors and editors are to be congratulated on having brought this excellent and comprehensive review to such a successful conclusion.

Field Crop Insects. By F. A. FENTON. The Macmillan Company, New York, 1952. Pp. 405, figs. 224. Price \$5.75.

The 17 chapters in this attractive book deal with insect abundance and distribution, the nature and use of insecticides, control by physical, mechanical, cultural, and biological means, plant quarantine and pest control campaigns, and leaf-destroying, sap-sucking, fruit-feeding, soil-inhabiting, and boring insects and those that feed on floral parts, seeds, and farinaceous material. The book is designed for use in a beginning course for agricultural students. The illustrations are well chosen and very useful in understanding the text. The control of soil-inhabiting insects, such as wireworms, white grubs, white-fringed beetles, corn rootworm, spotted cucumber beetle, seed-corn maggot, and ants, and the use of carbon bisulfide, naphthalene, ethylene bromide, and benzene hexachloride in connection therewith, are of special interest to soil scientists.

Geography of Latin America. THIRD EDITION. By FRED A. CARLSON. Prentice-Hall, Inc., New York, 1952. Pp. 569, figs. 151. Maps (in color) 4. Price, \$6.75.

The author dedicates this book to "Chris," his grandson, as testimony of his confidence in the youth of the Americas. One of his primary purposes is to establish a better understanding between the youth of the two continents in the western hemisphere. After dealing with the general heritage and evolution

of Latin America, each of the countries is considered separately, including all those in South and Central America, Mexico, and the West Indies. The relief and rainfall maps of South America are of special interest to soil-plant scientists. The agriculture of each country is concisely reviewed, but with sufficient detail to give the reader a good idea of its nature and importance. This is a very valuable book, which could be read to advantage by all those who are or should be interested in our neighbors to the south.

- ✓ *Principles of Plant Physiology*. By JAMES BONNER AND ARTHUR W. GALSTON. W. H. Freeman and Company, San Francisco, 1952. Pp. 499. Price \$5.50.

The material contained in this book is exceptionally well presented, the drawings by Evan L. Gillespie being especially meritorious and easily understood. The book is designed for use in a one-semester or two-quarter course. The method employed is one of dealing as concisely as possible with the theories involved, and selecting the most plausible explanation for development. Following an introductory chapter, the sequence is: photosynthesis, mineral nutrition, permeability, water, soil, translocation, enzymes, carbohydrates, respiration, nitrogen, lipids, metabolism, growth, auxins, reproduction, dormancy, differentiation, and environment. The book is entitled to wide adoption by teachers of plant physiology, and it will be found very useful for reference by other soil-plant scientists who need more information on this subject.

- Proceedings of the Twenty-Seventh Annual Meeting of the National Joint Committee on Fertilizer Application*. The National Fertilizer Association, Washington, D. C., 1951. Pp. 124. Paper-bound.

This report gives the program of the annual meeting, minutes of the executive committee, membership of subcommittees, and reports of the chairmen of subcommittees on small fruits, leaf analysis, fertilizer solutions, machinery for applying fertilizers, sweet corn, vegetable crops, new concepts on fertilizers, crop rotation, and transplanting solutions. This report, in conjunction with those of previous years, presents the changing status of the thinking of soil-plant scientists on the use of fertilizers for increasing crop production.

- Soil and Civilization*. By EDWARD HYAMS. Thames & Hudson, New York, 1952. Pp. 311, plates 4, maps 5.

The author has borrowed the title from Milton Whitney's book, which was published in 1925. He conceives of man as being largely a parasite or a disease of soils. For parasitism, he draws attention to the alluvial soils of the Tigris-Euphrates and Indus River valleys. For man as a disease, he considers the agricultural situation that preceded the fall of civilizations in Sparta and Rome, with a more modern example in Oklahoma. China, Eurasia, and India are classed as marginal cases. In contrast, the Incas and the farmers of Atlantic Europe are called "soil makers." The final chapter deals with matters of the spirit. One develops a sense of frustration in reading the book in the feeling that the author should have read further and fortified his concepts by extended field observations and more complete documentation. He speaks of low wheat yields

in dry-farming areas of America "obtained only with fertilizers," and he accepts Sir Albert Howard's concepts as his own. This is the interesting work of a philosopher who has made an important contribution to our thinking, but it is a mere beginning of the contribution that could and should be made on this subject.

✓ *Soil Testing in the United States.* The National Soil and Fertilizer Research Committee. F. W. PARKER, Secretary, Bureau Plant Industry, Beltsville, Maryland, 1951. Pp. 117. Paper-bound.

This report was prepared by the Soil-Test Work Group, consisting of W. L. Nelson, J. W. Fitts, L. T. Kardos, W. T. McGeorge, R. Q. Parks, and J. Fielding Reed. It gives the information that was assembled on extent of soil testing, sampling, equipment, tests made, techniques employed, interpretation of tests, recommendations to farmers, charges, and costs. A list of commercial soil-testing laboratories is appended and 103 pertinent references are given. This is the most comprehensive review of the subject ever presented. It merits careful study by those who are concerned with this subject.

Tractors and Their Power Units. By E. L. BARGER, W. M. CARLETON, E. G. McKIBBEN, AND ROY BAINER. John Wiley and Sons, Inc., New York, 1952. Pp. 496. Price \$6.50.

Four tractor specialists have joined forces in the writing of this well-presented and attractively illustrated book. The 26 chapters deal with the history and development of the tractor, power measurement, thermodynamic principles, internal combustion cycles, valves, fuels, carburetion, ignition systems, cooling systems, lubrication, dirt exclusion, governors, engine types and performance, design features, operator's comfort, mechanics of the chassis, hitches, clutches, drives, power take-off, traction, tests, maintenance, and power cost. References and problems are appended to each chapter. The book is well adapted for classroom purposes. It is of interest to note that a good bit of attention is given to the effect of the soil (dust) on the tractor but none on the effect of the tractor on the soil.

NEWS NOTE

AGRICULTURAL SPECIALISTS NEEDED

A large number of specialists in agricultural engineering, animal husbandry, entomology, plant pathology, horticulture, soils, and agronomy are needed to represent the United States in technical cooperation programs abroad. Employees must have had several years of successful professional experience and must be skilled in their professions. They are not required to take Civil Service examinations. They should be between 30 and 60 years old. Salary rates range from \$6,000 to \$11,000 a year. Persons interested are asked to submit Form 57, which may be obtained from First- and Second-Class Post Offices, or to write the Office of Personnel, U. S. Department of Agriculture, Washington 25, D. C.

SOIL SCIENCE

VOLUME 73

June 1952

NUMBER 6

SYNTHETIC SOIL CONDITIONERS

This issue of *SOIL SCIENCE* is devoted exclusively to a series of papers presented at a symposium on "Improvement of Soil Structure," which was held in Philadelphia, December 29, 1951, in conjunction with the meetings of the American Association for the Advancement of Science. Interest was centered around the subject of synthetic soil conditioners, with particular reference to certain polyelectrolytes that have been developed by the Monsanto Chemical Company and have been made available to the public under the trade name "Krilium." So much interest was developed in this general subject as a result of the symposium that it seemed desirable to make these papers available to all readers of this Journal.

FIRMAN E. BEAR

INFLUENCE OF ORGANIC MATTER ON AERATION AND STRUCTURE OF SOIL

J. H. QUASTEL

McGill University, Montreal

It is now well known that organic matter plays an essential role in securing in soil the structure, or tilth, that is required for high fertility. In fact, maintenance of the supply of organic matter to arable soils is of the greatest practical importance, for productive capacity is largely dependent upon it.

The organic matter of soil is primarily derived from the decomposition products of plants and from the products of autolysis of the vast microbiological population which develop at the expense of substances of plant origin. A dynamic equilibrium exists between the immense numbers and varieties of microorganisms that inhabit the soil and the organic matter being continually supplied by decaying animal and vegetable tissues. The equilibrium is such that the ratio of carbon to nitrogen in the soil remains remarkably constant, at about 10. Soil, therefore, normally contains an extensive range of substances commonly classed as metabolites of animal and plant tissues. The speeds of change of these substances may be very great, the rates depending on the temperature, hydrogen-ion concentration, aeration, water availability, and mineral content of the soil. A number of substances derived from animal, plant, or microbiological life are, however, relatively resistant to breakdown, and these substances make up, for the most part, what is commonly known as organic matter. Such substances have the physical and chemical properties that together help determine the structure and influence the fertility of a soil. These substances are also in a continuous state of change,

but an equilibrium is achieved so that their total quantity remains fairly constant in any one locale, the amount being largely dependent on climate and geographical conditions and the type of plant life being supplied.

Among the most characteristic of the products making up the soil organic matter is the black colloidal material known as humus, which has high hydrophilic power and the ability to make possible the crumb structure of soil so necessary for fertility. Humus is a complex mixture of substances, which was once thought to be formed solely from the cellulose in soil but is now known to be produced in at least the three following ways: (a) by bacterial attack on cellulose, (b) by chemical transformations of lignin, and (c) from fungal mycelia. Humic acid from soil is reported to contain about 5 per cent nitrogen; it cannot be wholly, therefore, a lignin or cellulose product. Humus must be regarded as a natural system varying in composition and consisting largely of derivatives of lignins, proteins, certain hemicelluloses, and even cellulose. It is not in a static condition but undergoes continuous change, involving syntheses and decompositions. According to Waksman and Iyer (20), the humus components consist of two groups of substances: (a) the lignoproteins combined with bases such as calcium, iron, and aluminum ions; these lignoproteins, probably combined with the hemicelluloses or the polyuronides form the fraction known as humic acid and are responsible for the characteristic color and for some of the organic colloidal properties of soil; and (b) the cellulose, hemicelluloses, waxes, fats, and starches in various amounts and proportions according to the location; for example, forest soils, highland peats.

Aggregating substances are uniformly distributed in soil crumbs. They consist, according to Kroth and Page (12), of polar organic substances, resulting from the decomposition of fresh organic matter, and of a group of substances, including iron and aluminum oxides, fats, waxes, and resins, that are less efficient as soil aggregators. Bacterial slimes and fungal mycelia, it is well known, play an important role in soil aggregation and resistance of soils to erosion (9, 16).

EFFECTS OF POLYURONIDES AND POLYSACCHARIDES ON SOIL AGGREGATION

It is now apparent that among the humus constituents are the polyuronides and uronic groupings, and these are widely distributed in plants, composts, and soils. Bartholomew and Norman (1), who have worked out a method of estimating uronic acids in soils, have shown that the uronic acid content varies with the type of soil. There is indeed a relationship between the uronic acid content and soil fertility. The polyuronides present include such well-known substances as pectic acid and alginic acid and a variety of bacterial polysaccharides. Pectic acid is composed of D-galacto-pyruonic acid residues mutually united by 1:4 α -linkages. Alginic acid, on the other hand, is composed of a chain of D-mannopyruonic acid residues joined by 1:4 β -linkages. The formulas of both polyuronides resemble that of cellulose. The specific polysaccharides of bacteria, for example, *Pneumococci* Type III, are polyuronides; in many cases the uronic acid constituent has not been identified with certainty. Many mucilaginous polysaccharides contain uronic acid units, and it is known that complex polyuronides compose

the plant gums found in soils containing decaying vegetable matter. Forsyth (6) has isolated from soil a polysaccharide fraction containing uronic acid units.

Polysaccharides which are metabolic products of bacteria and which are known to improve the aggregating properties of soils are the levans and dextrans. The levans, which on hydrolysis yield fructose, are formed from sucrose by commonly occurring soil organisms such as *B. subtilis*. These organisms are able to secrete an enzyme that accomplishes the synthesis (11).

Following work by Martin and Waksman (13) on the binding action of mycelia and organic matter on soil particles, Martin (14, 15) showed that addition of cultures of *B. subtilis* to soil produces aggregations of soil particles due to the formation of organic substances as a result of growth of the organism on a molecule such as sucrose. He demonstrated that addition of bacterial polysaccharides such as the levans and dextrans will affect soil structure to a greater degree than will addition of casein or of lignin. Geoghegan and Brian (7, 8) have found that bacterial and other polysaccharides aggregate soils. They reported that bacterial levans and dextrans have marked aggregating effects on soil particles, the levans being formed by a wide variety of aerobic organisms, and the dextrans being formed by various species of *Leuconostoc*. Soil crumbs containing small quantities of levans are very stable but are eventually broken down by bacterial action. The aggregating action of the products derived from microorganisms is much greater than the direct binding effect of the microbial cells themselves. As soil aggregators, dextrans, produced from sucrose by the metabolic action of *Leuconostoc*, are apparently superior to the levans, derived from sucrose by the action of *B. subtilis*. A polysaccharide formed by *Rhizobium* and containing 67 per cent glucose and 20 per cent uronic acid residues (2) is a less efficient soil aggregator than either the levans or the dextrans. Undoubtedly, the structure of the polysaccharide or polyuronide has a strong influence on the aggregating properties of soil. Hydrogen bonding is considered a major mechanism whereby polysaccharides are bound to the soil particle.

Haworth, Pinkard, and Stacey (10) have shown that poor soils with a low total organic content have only traces of polysaccharides; those with higher total organic content have 0.5–1.5 gm. polysaccharide per kilogram moisture-free soil and possess a greater moisture-retaining capacity. Polysaccharide fractions containing levans were isolated from such soils. Swaby (19), in recent work on the influence of humus constituents, showed that a variety of substances, including proteins and polyuronides, affect soil aggregation.

EFFECT OF ALGINIC ACID ON SOIL AERATION

Soil aggregation is of the greatest importance for soil fertility, in allowing living cells, including plant roots, to obtain sufficient oxygen and water for their optimal metabolism.

The marked effect of alginic acid in increasing soil aeration by improving the water-holding power and crumb stability was first shown by Quastel and Wobley (18). These investigators devised a *direct* method of assessing the availability of oxygen to living cells, such as those provided by microorganisms or plant roots,

which are present in soils. This availability decreases after a critical amount of water has been added to soil, because the crumb pores become blocked, and oxygen cannot obtain access, except at a very diminished rate, to the cells surviving in the pores. Before this critical state is reached, a soil with high water-holding power will take up much more water than one with low water-holding power.

The technique adopted by Quastel and Webley (18) is based upon the employment of the Warburg manometric apparatus commonly used in biochemical investigations on cell respiration. A brief description of the method they used follows:

A standard quantity (usually 4 gm.) of a crumbed and sieved air-dried soil (1-2-mm. fraction) is placed in the flask of a Warburg respiratory vessel. A known quantity of a suspension of microorganisms of known respiratory activity, in presence of excess nutrients, is spread over the crumbs as evenly as possible. The rate of oxygen uptake at 37°C. by the microorganisms is measured (for half

TABLE 1
Aeration factors (A.F.) of soils containing alginate

	A.F. VALUES AT VARIOUS SOIL* MOISTURE CONTENTS			
	25% H ₂ O	37.5% H ₂ O	50% H ₂ O	62.5% H ₂ O
Standard soil alone (a heavy clay depleted of organic matter).....	82.7	48.6	29.4	14.9
Standard soil containing 0.1% Na alginate.....	88.4	76.4	42.7	17.2
Standard soil containing 0.25% Na alginate.....	90.0	82.7	51.4	20.6
Standard soil containing 1.0% Na alginate.....	97.4	96.3	67.9	39.0
Garden soil.....	—	101.0	83.2	72.0
Garden soil treated with 1% Na alginate.....	—	108.4	112.0	113.4

* Based on dry weight of soil.

an hour) in the usual way, though there is no necessity to shake the manometers. If, after the suspension of microorganisms has been spread over the soil crumbs at a certain water content, oxygen consumption by the organisms is found to be equal, within the experimental error, to that of organisms examined under optimal respiratory conditions in absence of soil, aeration of the soil is held to be optimal at that water content. If, on the other hand, the respiration of the organisms spread over the soil crumbs is a fraction ($1/n$) of that obtained under optimal respiratory conditions, aeration of the soil is said to be a fraction ($1/n$) of the optimum. The fraction ($1/n$) expressed as a percentage of the optimum value, is defined as the aeration factor (A.F.) of the soil. Thus, an A.F. of 100 indicates optimal aeration; an A.F. of 50 indicates half optimal aeration. It is possible, therefore, from measurements of the oxygen consumptions of suspensions of test organisms spread over soil crumbs at different water levels to obtain values of the aeration of soils, expressed as A.F., at these water levels. Curves may be plotted showing the relation between the A.F. and the water content of a soil.

A convenient test organism is baker's yeast, suspensions of which in a glucose

solution may be easily prepared. A description of the rates of oxygen consumption by yeast suspensions spread over soil crumbs and how these rates vary with the water content of the soil is given by Ellinger and Quastel (3).

It is found that addition of sodium alginate to a soil greatly increases the amount of water that may be added to the soil before the availability of oxygen (defined as the aeration factor) falls. Typical results obtained by Quastel and Webley (18) on a soil depleted of organic matter are shown in tables 1 and 2. Addition of alginate to a garden soil with a fairly high content of organic matter and showing good aeration at high water content improves the hydrophilic properties (table 1). It was calculated in one series of experiments that addition of 0.1 gm. sodium alginate to 100 gm. air-dried soil had a gross effect equivalent to an increase of 11 per cent in water-holding power. It was also shown that crumb stability is improved by the alginate addition.

TABLE 2
Water-holding power of soil containing alginate

Na ALGINATE CONTENT	WATER CONTENT OF STANDARD SOIL PER DRY WEIGHT SOIL FOR A.F. 50
<i>per cent</i>	<i>per cent</i>
0	36
0.1	47
0.25	51
0.75	55
1.0	58.5

EFFECTS OF CELLULOSE ESTERS ON SOIL AERATION

Not only is the polyuronide effective in improving the soil structure; cellulose esters such as cellulose acetate, methyl cellulose, and carboxymethyl cellulose will improve the air-water relationships of a soil (table 3). These results confirm the findings of Felber and Gardner (4, 5) that addition of methyl cellulose to soil brings about a considerable retention of moisture.

Addition of farmyard manure and horse dung greatly improves the air-water relationships and the crumb stability of soil. Results obtained by Quastel and Webley (18) are shown in table 3. Seemingly the effects of addition of these materials are twofold: (a) physical, due to the presence of fine straw which helps to bind the soil crumbs together, and (b) chemical, or physicochemical, due probably to the presence of polyuronides or polysaccharides affecting the hydrophilic properties of the clay particles.

Addition of sewage sludges, composts, and refuse to soil improves the air-water relations generally in proportion to the amount of organic matter present. Extracts of soils and peats may also be effective, probably in accordance with their content of polyuronic acids (table 3).

Though these observations have shown clearly that the commonly occurring forms of organic matter in soil and in natural manure, such as polyuronides and also polysaccharides, greatly improve the hydrophilic properties and crumb

stability of soils, use of such substances is dependent on the rate at which they decompose in soil and lose their improving properties. That the addition of alginate to a soil may improve the yield of a tomato crop grown under glass has been shown by Quastel and Webley¹ and confirmed by Owen (17), but it is certain that the fairly rapid breakdown of the polyuronide in soil militates against its use on a wide scale as a soil improver.

It is questionable, moreover, whether the polysaccharides are likely to offer any advantages over polyuronides as possible soil improvers. Both these groups of molecules, which may confer high-aggregating powers on soil and which are

TABLE 3
Aeration factors (A.F.) of soils containing various conditioners

	A.F. VALUES AT VARIOUS SOIL* MOISTURE CONTENTS			
	25% H ₂ O	37.5% H ₂ O	50% H ₂ O	62.5% H ₂ O
Standard soil alone.....	86.4	55.1	27.0	16.0
Standard soil + 1% cellulose acetate.....	97.1	89.2	58.6	31.7
Soil + 1% methyl cellulose (low viscosity).....	91.7	88.8	53.7	21.5
Soil + 1% carboxymethyl cellulose.....	100.4	94.3	52.6	25.6
Soil + 2% farmyard manure (fresh).....	90.4	73.1	46.2	22.2
Soil + 2% farmyard manure (air-dried and ground).....	86.2	69.6	32.5	12.6
Soil + 2% horse dung (fresh).....	104.0	107.5	83.7	76.1
Soil + 2% horse dung (fresh but well washed with water).....	92.4	95.4	70.0	54.3
Extract from 100 gm. garden soil mixed with 100 gm. stand- ard soil.....	83.6	92.2	62.6	28.9
Soil + 2% extract of garden soil.....	109.4	123.5	86.8	35.3
Soil + 2% ground peat.....	88.2	68.1	36.5	18.5
Soil + 2% extract of peat.....	100.5	94.8	56.9	24.5

* Based on dry weight of soil.

nearly related to each other chemically, are metabolites in the sense that they are built up and broken down by biological means. The speeds of decomposition depend on the availability of nitrogenous and phosphorus-containing compounds, on aeration, on temperature, on water availability, and on pH; in short, on the same factors that greatly determine the nutrition of the plant.

SYNTHETIC SOIL CONDITIONERS

Knowledge of the mechanism of action of these naturally occurring substances that improve soil structure should give us a clue to methods of synthesizing substances with a similar mechanism but with a relatively slow rate of destruction in the soil. Such synthetic substances should, like the naturally occurring ones, be devoid of toxic effects on plant or animal. They should not interfere with the

¹QUASTEL, J. H., AND WEBLEY, D. M. Unpublished data. 1945.

soil microbiological equilibria involving for example, the growth of nitrogen-fixing organisms. They should not remove the trace elements important for plant nutrition. It has always seemed to the author that macromolecules, of a size comparable with those of the polyuronides, of a chemical nature that allows a combination with the soil particles similar to that produced by the polyuronides, so that hydrophilic and aggregating qualities may be acquired, but which are so constituted as to withstand rapid breakdown by biological or other means, are the types of substances which would be ideal for improvement of soil structure on an extensive scale. How this ideal has been to a great extent achieved by the work of the Monsanto scientific staff, with whom the author has had the privilege of being associated, is shown in the following papers.

REFERENCES

- (1) BARTHOLOMEW, W. V., AND NORMAN, A. G. 1941 Determination of uronic groups in soils and plant materials. *Iowa State Col. Jour. Sci.* 15: 253-260.
- (2) COOPER, E. A., DAKER, W. D., AND STACEY, M. 1938. Enzyme formation and polysaccharide synthesis by bacteria. *Biochem. Jour.* 32: 1752-1758.
- (3) ELLINGER, G., AND QUASTEL, J. H. 1948 Preliminary experiments in the study of the respiratory activity of microorganisms suspended in thin films of fluid adhering to solid surfaces. *Biochem. Jour.* 42: 214-218.
- (4) FELBER, I. M. 1944 Moisture conserving effect of methyl cellulose in soil. *Amer. Soc. Hort. Sci. Proc.* 45: 331-337.
- (5) FELBER, I. M., AND GARDNER, V. R. 1944 Effect of a hydrophilic colloid of high viscosity on water loss from soils and plants. *Mich. Agr. Exp. Sta. Tech. Bul.* 189: 3-30.
- (6) FORSYTH, W. G. C. 1947 Studies on the more soluble complexes of soil organic matter. *Biochem. Jour.* 41: 176-181.
- (7) GEOGHEGAN, M. J., AND BRIAN, R. C. 1946 Influence of bacterial polysaccharides on aggregate formation in soils. *Nature* 158: 837.
- (8) GEOGHEGAN, M. J., AND BRIAN, R. C. 1948 Aggregate formation in soils: I. *Biochem. Jour.* 43: 5-14.
- (9) GILMOUR, C. M., ALLEN, O. N., AND TRUOG, E. 1949 Soil aggregates as influenced by the growth of mold species, kind of soil and organic matter. *Soil. Sci. Soc. Amer. Proc.* (1948) 13: 292-296.
- (10) HAWORTH, W. N., PINKARD, F. W., AND STACEY, M. 1946 Function of bacterial polysaccharides in the soil. *Nature* 158: 836-837.
- (11) HESTRIN, S., AND AVINERI-SHAPIRO, S. 1944 Mechanism of polysaccharide production from sucrose. *Biochem. Jour.* 38: 2-10.
- (12) KROTH, E. M., AND PAGE, J. B. 1947 Aggregate formation in soils with special reference to cementing substances. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 27-34.
- (13) MARTIN, J. P., AND WAKSMAN, S. A. 1940 Influence of microorganisms on soil aggregation and erosion. *Soil Sci.* 50: 29-47.
- (14) MARTIN, J. P. 1945 Microorganisms and soil aggregation: I. *Soil Sci.* 59: 163-174.
- (15) MARTIN, J. P. 1946 Microorganisms and soil aggregation. II. Influence of bacterial polysaccharides on soil structure. *Soil Sci.* 61: 157-166.
- (16) MISHUSTIN, E. N., AND GROMYKO, E. P. 1946 Stability of soil macroaggregates formed by microorganisms. *Mikrobiologiya* 15: 169-175.
- (17) OWEN, O. 1947 Use of sodium alginate in composts for propagating tomatoes. *Cheshunt Exp. Res. Sta. Ann. Rpt.* 1947: 104-106.
- (18) QUASTEL, J. H., AND WEBLEY, D. M. 1947 Effects of the addition to soil of alginic acid and other forms of organic matter on soil aeration. *Jour. Agr. Sci.* 37: 257.

- (19) SWABY, R. J. 1950 Influence of humus on soil aggregation. *Jour. Soil Sci.* 1: 182-191.
- (20) WAKSMAN, S. A., AND IYER, K. R. N. 1932 Synthesis of humus nucleus, an important constituent of humus in soils, peats and composts. *Jour. Wash. Acad. Sci.* 22: 41-50.

EFFECT OF SYNTHETIC POLYELECTROLYTES ON AGGREGATION, AERATION, AND WATER RELATIONSHIPS OF SOIL

R. M. HEDRICK AND D. T. MOWRY¹

Central Research Laboratories, Monsanto Chemical Company

As discussed elsewhere in this issue, the role of polyuronides and possibly other polysaccharides of bacterial origin in stabilizing soil structure has been gradually elucidated in recent years by Martin, Quastel, Fuller, Webley, Forsyth, Geoghegan, Swaby *et al.* (10, 11, 12, 18, 19, 20, 23, 25, 26).

In our own experience and in that of others (20, 21, 22, 23), attempts to ameliorate poor soil structure by addition of naturally occurring polyuronic acid salts and other closely related polysaccharides have not been successful or practical even though soil aggregation was improved. There are three reasons for this: (a) The relatively large amounts required for significant improvement in structure (5 to 10 tons per acre) cause harmful effects through the large quantities of cations released, whether these be sodium, potassium, or ammonium ions; (b) the large amount of rapidly decomposable organic material introduced causes denitrification and at least temporary unavailability of other plant nutrients, an effect that presumably can be neutralized by the concomitant addition of requisite nutrients; (c) the rapid decomposition of added polysaccharide derivatives (2 weeks to 2 months) by soil microorganisms renders such methods uneconomical.

A number of other chemicals not known to occur in natural soils have been proposed as agents for improvement of soil structure. Methyl cellulose (8, 13, 23) and carboxymethyl cellulose salts (13, 23) have a moderately high aggregate-stabilizing effect. They resemble the polyuronides and other polysaccharides, however, in their susceptibility to rapid decomposition by soil microorganisms.

In some soils sodium silicate (14) and potassium silicate (5) are reported to give excellent stabilization of soil crumbs at relatively high levels of application (0.25 to 1.0 per cent). In another investigation (15), although temporary improvements in workability, but not porosity, were reported, the initial yield improvements were attributed to changes in nutrient availability. Preliminary work with sodium silicate at these high levels in this laboratory indicates a toxic effect on soil microflora. At lower dosage (0.1 per cent or less), the aggregating effect was not significant.

Treatment of soil crumbs with dimethyldichlorosilane gas at dosages of 0.2 to 0.5 per cent is reported to cause moderate increases in the percentage of water-stable crumbs larger than 0.25 mm. (27). This behavior was confirmed in the present study. The difficulties in application of a gas of high animal toxicity militate against its practical use. The stability, moreover, was conferred primarily by a waterproofing action as evidenced by an obvious reduction in the rate of wetting of the soil crumbs when placed in the Yoder wet-sieving apparatus (30).

¹ The authors are indebted to Norman Phillips, J. G. Villars, and J. M. Deming for assistance in much of the experimental work; to R. G. Anderson, M. Baer, and E. L. Ringwald for synthesis of many of the polymers; and to J. H. Quastel for his interest and advice.

Aggregate stability in this case was achieved at the expense of water-holding capacity as measured by determinations of the moisture equivalent (see table 6). Considerable increases in water-stable aggregates can be obtained by a large number of waterproofing chemicals such as stearic acid (17) and abietic acid (29). General experience in this laboratory, however, is that materials of a waterproofing type reduce germination of seed and sometimes hinder normal growth of plants because of unfavorable soil-moisture relationships.

This paper presents the results of a program of several years' duration in which various chemicals were evaluated for their effect on aeration and aggregation of soil. As primary screening methods the Warburg technique of Webley (28), as modified by Ellinger and Quastel (6), and the wet-sieving procedure of Yoder (30) were used. Although most previous investigators were primarily concerned with chemicals that closely resembled the polyuronides and other humus components in chemical structure, the present investigation followed a more empirical approach in that a large variety of materials were examined without regard to chemical structure. More than 700 chemicals have been screened to date, most of which were synthesized in these laboratories.

It soon became apparent that certain water-soluble, polymeric electrolytes² of high molecular weight and optimum configuration were effective in the extremely low concentrations desired. Because of economic and practical considerations, the two materials on which most of the work has been carried out are CRD-189, the sodium salt of a hydrolyzed polyacrylonitrile, and CRD-186, another carboxylated polymer which has a higher tolerance for calcium ion and can be formulated as a partial calcium salt. Further details on chemical syntheses of these and other materials tested will be published elsewhere.

MATERIALS AND METHODS

Soil types

Most of the experimental work reported here was on Miami silt loam obtained near Dayton, Ohio. This soil contained 22.2 per cent clay, 46.6 per cent silt, and 31.2 per cent sand. A local alluvial sandy loam containing 19.0 per cent clay, 33.8 per cent silt, and 47.2 per cent sand was also used, as were a number of other soils reported in table 5.

Procedures

Soil was prepared for evaluation in the Warburg apparatus as described by Quastel and Webley (23). To 100 gm. air-dried soil pulverized to pass a 1-mm. sieve was added 30 ml. of water containing the desired quantity of chemical to be added. Water-insoluble materials were mixed with dry soil, and then 30 ml. of water was added. After the water had soaked in, the soil was mixed thoroughly with a spatula. If the soil was still crumbly, sufficient water was added to bring it to the sticky point. After air-drying, the soil was broken up, and 2-4-mm. crumbs were collected. Four-gram portions of crumbs were placed in Warburg

² The soil conditioners discussed in this paper are commercially known by the trade name "Krilium."

flasks. Equal amounts of yeast and glucose were suspended in appropriate amounts of water and added to the soils. The oxygen consumed by yeast at four levels of soil moisture was measured manometrically.

Soil crumbs were prepared for wet-sieving analysis by a different procedure. For comparative evaluation of chemicals the soil was pulverized to pass a sieve with 0.25-mm. openings. All natural aggregates larger than this size were thus destroyed and stones and debris were removed. The chemical to be added was mixed with the dry soil or dissolved in sufficient water to add 30 per cent moisture to the soil. The moist soil was then pressed through a 4-mm. sieve to form crumbs of a uniform size as described by Geoghegan and Brian (12). Forty-gram portions of crumbs were wet-sieved by the method of Yoder (30), using sieves with 0.84-, 0.42-, and 0.25-mm. openings.

Soil for greenhouse experiments was treated in a number of ways, generally by applying the chemical in sufficient water to raise the moisture content of the soil to that of optimum workability. Either dry or moist soil can be treated by this method. An alternative method was to mix the dry chemical with fairly dry soil and then add water to optimum workability.

Field treatments were usually best made by spreading the chemical on the dry surface of a previously prepared seedbed before incorporating it to the desired depth with a rotary tiller. Polyelectrolytes were mixed into the soil most efficiently when the soil was fairly dry. In wet soil, the mixing was slightly less efficient because the polymer became gummy as it adsorbed moisture and resisted dispersion. Subsequent addition of water by rainfall or artificial means dissolved the chemical and further distributed it to each soil crumb, where it was adsorbed.

The rate of infiltration and percolation through undisturbed soil was measured on 3-inch cores. The cores were allowed to adsorb water by capillarity overnight. Then the rate of percolation through the core was measured while a 1-inch head of water was maintained.

The moisture equivalent of soil samples was determined by the suction method of Bouyoucos (3) and also by the centrifuge method. In the latter method 5-gm. samples of soil were allowed to soak in water overnight and then centrifuged for a half-hour at a speed giving a force 1,000 times that of gravity.

The wilting percentage was determined by the method of Breazeale and McGeorge (4) using soil in glass jackets on the stems of tomato plants. A trace of a rooting powder on the stem was found to hasten the emergence of roots into the soil sample.

The rate of evaporation was determined by placing 4-pound samples of control soil and 0.05 and 0.1 per cent treatments in large beakers at 23 per cent moisture. The bulk density was equalized by tapping the beaker. The beakers were placed on a greenhouse bench and weighed at intervals of 2 or 3 days to follow the loss of moisture by evaporation.

RESULTS AND DISCUSSION

Aeration measurements by the Warburg technique

Graphical representation of some typical results of Warburg investigations in figure 1 indicate the magnitude of improvements in soil aeration possible through

chemical treatment. Good aeration can be maintained at high water levels with large amounts of peat and manure, which provide both a physical bulking effect, and the bonding action of natural polyuronides. Nearly equivalent results are given by sodium alginate at the 1 per cent level or CRD-186 at the 0.05 to 0.1 per cent levels. The oxygen demand of the native microflora is shown in the blank curve without yeast, and this respiration accounts for the aeration factor values in excess of 100 recorded for some of the treatments. Reduction or elimination of the blank by some chemicals such as sodium silicate or trimethylol melamine resin (table 1) indicates undesirable toxicity to soil microflora. The latter compound also greatly inhibited yeast metabolism.

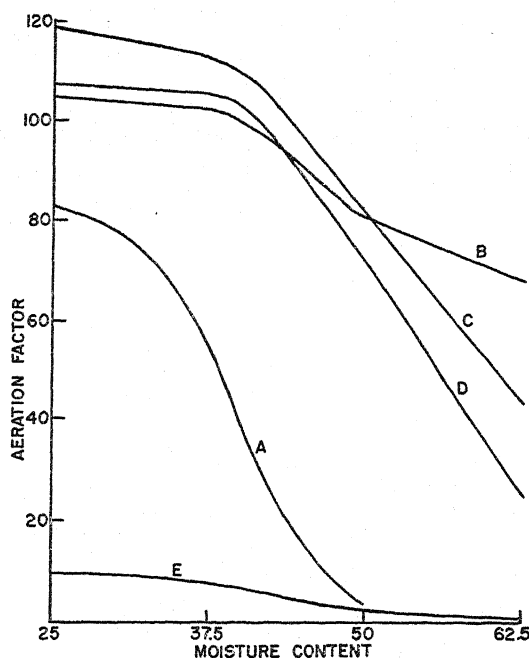


FIG. 1. AERATION FACTORS FOR A STANDARD SOIL CONTAINING CHEMICAL ADDITIVES

A. Untreated alluvial sandy loam. B. Potting soil containing 20 per cent rotted manure and 20 per cent peat. C. Sandy loam + 0.1 per cent CRD-186. D. Sandy loam + 1.0 per cent sodium alginate. E. Untreated soil without yeast (blank value).

Chemical additives, such as sodium abietate, which stabilized the soil through a waterproofing action usually reduced the aeration factor to 40 or 50 at the low water levels but maintained about the same value up to 62.5 per cent moisture. Consistent improvement in aeration at all water levels is indicated by CRD-186 at the 0.1 per cent level, as shown by the data in table 2 for four additional soils.

Aggregate stability as measured by wet-sieving

Experience soon indicated that the primary beneficial property being measured by the Warburg technique was the stability of crumbs to the slaking action of

water. This factor was measured directly, as well as more easily and reproducibly, by a conventional wet-sieving procedure. Of a number of chemicals cited earlier which have been suggested as agents for the improvement of soil structure (table 3), only high molecular weight polysaccharide derivatives had significant aggregate stabilizing activity at dosages of 0.1 per cent or less. The only exception was a strongly waterproofing agent such as sodium abietate, which prevented

TABLE 1
Warburg aeration in sandy loam

CHEMICAL ADDED	CONC.	AERATION FACTOR AT FOUR H ₂ O LEVELS			
		25%	37.5%	50%	62.5%
	%				
None.....	—	83	55	0*	0
Sodium alginate.....	1.0	108	106	73	26
Sodium alginate.....	0.25	122	95	52	0
Sodium alginate.....	0.1	118	85	28	0
Sodium carboxymethyl cellulose.....	1.0	103	98	63	7
Pectin.....	1.0	86	77	0	0
Lignin.....	1.0	90	67	0	0
Sodium silicate†.....	1.0	94	79	56	20
Trimethylol melamine‡.....	1.0	13	12	2	0
CRD-186.....	1.0	130	99	63	30
CRD-186.....	0.1	128	92	66	40
CRD-189.....	0.1	113	99	72	35

* Negative readings from swelling of the soil because of trapped CO₂ are also recorded as zero readings.

† Caused 60 per cent reduction in respiration of soil microflora.

‡ Caused 95 per cent reduction in blank.

TABLE 2
Warburg aeration in four soils

SOIL	AERATION FACTOR AT FOUR H ₂ O LEVELS			
	25%	37.5%	50%	62.5%
Miami silt loam (Ohio).....	82	68	8	0
Miami silt loam + 0.1% CRD-186.....	106	86	45	11
Paulding clay (Ohio).....	94	92	64	0
Paulding clay + 0.1% CRD-186.....	105	102	85	57
Grenada silt loam (Tenn.).....	83	69	46	0
Grenada silt loam + 0.1% CRD-186.....	99	103	99	76
Memphis silt loam (Tenn.).....	92	80	56	0
Memphis silt loam + 0.1% CRD-186.....	104	100	82	51

the interior of the crumbs from becoming thoroughly wetted during the standard half-hour test. Dimethyldichlorosilane stabilized crumbs by a similar mechanism, but a 0.2 per cent dosage was required to effect a 13 per cent increase in aggregation. Of all the chemicals tested in our studies, only high molecular weight polyelectrolytes such as CRD-186 and CRD-189 caused substantial increases in water-stable aggregates at dosages of 0.01 to 0.02 per cent.

Aggregate size distribution is affected by dosage of CRD-189 as shown in table 4. As would be expected, the quantity of large crumbs increased markedly with heavier application of the conditioner. CRD-186 gave similar results.

Results of laboratory applications of CRD-186 to 23 structurally deficient soils are shown in table 5. A correction was made for primary particles larger than 0.25 mm., and the stability data given are based only on the fraction smaller than 0.25 mm. All treatments were made at a moisture content of 30 per cent,

TABLE 3

Per cent water-stable aggregates >0.25 mm. given by four levels of addition of chemicals to Miami silt loam

CHEMICAL ADDED	WATER-STABLE AGGREGATES AT FOUR LEVELS OF CHEMICALS			
	0.1%	0.05%	0.02%	0.01%
	%	%	%	%
Sodium alginate.....	42	6	2	0
Methyl cellulose.....	14	—	—	1
Sodium carboxymethyl cellulose (high visc.)..	28	—	3	—
Sodium carboxymethyl cellulose (low visc.)..	11	—	1	—
Calcium lignin sulfonate.....	2	—	—	—
Humic acid (from coal).....	3	—	—	—
Gypsum.....	0	—	—	—
Sodium silicate.....	15	7	—	2
Sodium abietate*.....	96	—	—	12
CRD-186.....	96	84	70	50
CRD-189.....	92	72	42	16

* Caused severe waterproofing.

TABLE 4

Distribution of water-stable aggregate sizes at various concentrations of CRD-189

CONCENTRATION OF POLYMER	WATER-STABLE AGGREGATES			
	>0.84 mm.	0.84-0.42 mm.	0.42-0.25 mm.	Total > 0.25 mm.
%	%	%	%	%
0.005	0.0	0.0	2.0	2.0
0.01	1.8	4.7	9.0	15.5
0.02	4.5	21.5	16.2	42.2
0.05	54.0	12.8	5.0	71.8
0.1	82.3	5.0	4.7	92.0

which was not necessarily optimum for each soil. All the soils gave a positive response to treatment except Portsmouth fine sandy loam, which appeared to be very poorly wettable in its natural state and which had the highest amount of organic matter (4.6 per cent carbon) in the series. The degree of response did not seem to be correlated with pH, which ranged from 4.4 to 9.5, or with soil texture.

Workability

Very pronounced improvement in the workability of all soils treated with CRD-186 and CRD-189 was noted. The stickiness of clay soils was greatly re-

duced. They became crumbly and friable even at high moisture levels. The difference was especially noticeable in field plots after wintering. In addition to increased aggregation, treated soils showed marked increases in the lower plastic limit, and both factors probably contributed to workability improvement.

TABLE 5

Particles <0.25 mm. aggregated into water-stable aggregates >0.25 mm. by treatment with CRD-186

SOIL*	pH	PRIMARY PARTICLES >0.25 MM.	AGGREGATION		
			Untreated	0.02% CRD-186	0.1% CRD-186
		%	%	%	%
Paulding clay.....	6.0	5.5	26	29	63
Houston clay.....	7.8	3.2	8	8	37
Fargo clay.....	6.3	0.7	22	36	70
Sacramento clay.....	7.4	0.0	8	25	47
Panoche silty clay.....	7.6	16.9	7	15	34
Decatur silty clay.....	7.6	9.2	49	31	61
Brookston silty clay.....	6.5	4.2	28	42	72
Miami silt loam.....	5.8	9.3	7	48	96
Clarksville silt loam.....	4.4	15.5	14	29	83
Grenada silt loam.....	4.4	0.0	11	31	69
Hagerstown silt loam.....	5.8	3.3	32	58	81
Hammerly silt loam.....	7.6	14.8	4	15	31
Cherokee silt loam.....	6.1	2.0	7	34	94
Memphis silt loam.....	5.0	0.6	19	43	71
Pond loam.....	9.5	18.1	1	38	87
Chester loam.....	5.2	10.5	23	74	86
Jefferson loam.....	5.4	17.7	4	33	75
Renville loam.....	6.4	15.1	5	13	57
Portsmouth fine sandy loam....	4.5	—	66	38	36
Maumee fine sandy loam.....	7.0	3.7	27	29	64
Cecil sandy loam.....	4.8	46.3	78	86	74
Barboursville sandy loam.....	5.6	61.7	11	78	86
Lakeland sand.....	4.8	56.4	3	8	39
Ave.....	—	—	20	37	66

* Soil samples furnished by Garth Volk, Ohio State University; Victor J. Kilmer, U. S. Department of Agriculture; John N. Fiske, University of California; Nathan I. Brown, Soil Conservation Service, Nashville, Tenn.; Verlin H. Peterson, Kansas State College; J. D. Axtell, University of California; F. B. Smith, University of Florida.

Moisture relationships

Percolation rates. Although the primary effect of the polyelectrolytes was on aggregate stability, a number of secondary benefits of treatment accrue. Freshly treated soil crumbs, when placed in glass columns in the laboratory, may show hundredfold improvements in percolation rates over control crumbs of similar size if the original soil was heavy and in very poor tilth. Even in a fairly porous soil such as the sandy loam at Dayton, considerable improvements were noted. These field plots were treated with 0.05 per cent CRD-186 in June 1950. Undis-

turbed 3-inch core samples, taken in triplicate in May 1951, allowed a rate of percolation averaging 4.4 times that of the average of cores from adjacent control plots. Aggregate analysis at the time of sampling showed 44 per cent stable aggregates larger than 0.25 mm. in the treated plots compared to 16 per cent in the control plots.

Moisture equivalent. Treatment with polyelectrolytes also affected the moisture equivalent. Table 6 indicates that both CRD-186 and CRD-189 increased the moisture equivalent of soil treated in the laboratory. The Bouyoucos method gave larger increases than did the centrifuge method possibly because, in the very highly aggregated soil, the discontinuous capillary pores did not drain readily under suction. The increase in water held is 20 to 70 times the weight of the polyelectrolyte added. Hence, it is believed that the increase is primarily a result of improved structure rather than a result of association of water with the polymer itself.

TABLE 6
Effect of soil conditioners on moisture relationships in Miami silt loam

CHEMICAL ADDED	CONC.	MOISTURE EQUIVALENT		WILTING POINT
		Bouyoucos	Centrifuge	
	%	%	%	%
None.....	—	24.2	21.8	8.2
CRD-186.....	0.1	27.6	22.9	8.2
CRD-186.....	0.05	27.1	—	—
CRD-186.....	0.02	24.6	—	—
CRD-189.....	0.1	31.2	23.7	8.4
CRD-189.....	0.05	28.1	—	—
CRD-189.....	0.02	25.0	—	—
Dimethyldichlorosilane.....	0.2*	21.2	—	—

* Soil was waterproofed.

In contrast to soils treated with large amounts of peat moss (9), the permanent wilting percentage was not increased within experimental error by the treatment with polyelectrolytes. It is assumed, therefore, that all increase in water held by the soil is available for plant growth.

Chemicals such as rosin derivatives and dimethyldichlorosilane, which stabilized soil aggregates by a waterproofing effect, on the other hand, lowered the moisture equivalent. Such materials should, therefore, be undesirable agriculturally because aggregate stability is achieved at the expense of water-holding capacity.

Evaporation rate. In contrast to increased evaporation rates resulting from incorporation of peat moss or plant residues (9), treatment of soil with polyelectrolytes resulted in a reduction in the rate of surface evaporation (fig. 2). For example, it took 15 days for the control soil to lose half its water compared to 35 days for the soil treated with 0.1 per cent of CRD-186. This reduction is comparable in magnitude to that reported by Felber (8) for 1-2 per cent addi-

tions of solid methyl cellulose to a sandy loam. This effect is in agreement with the findings of Eser (7), who sieved soil into various aggregate fractions and determined that soil containing large crumbs lost water by evaporation much more slowly than did soil made up of small crumbs. In a well-aggregated soil, capillary pores are not so continuous as in a slaked soil, and water is therefore not brought to the surface by capillary action as fast as it can evaporate. The surface of a treated soil dries off more quickly, producing a mulching effect similar to that of cultivation. Treated soil does not form cracks and fissures which allow water vapor to escape from subsoil areas.

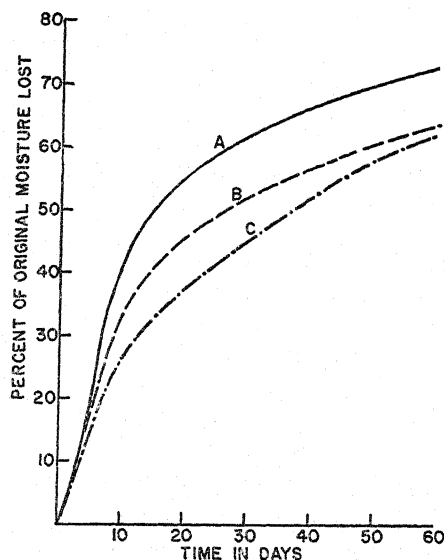


FIG. 2. EFFECT OF TREATMENT WITH CRD-186 ON RATE OF EVAPORATION OF WATER FROM MIAMI SILT LOAM

A. Untreated. B. Treated with 0.05 per cent CRD-186. C. Treated with 0.1 per cent CRD-186.

Effective life of polyelectrolytes in soil

Bacterial attack. To determine the effective life of polymer-treated aggregates under accelerated laboratory conditions, the percolation apparatus of Lees and Quastel (16) as modified by Audus (1) was used. Crumbs of soil treated with 0.1 per cent CRD-186 have remained stable under constant perfusion with water and air for 32 months at 76°F., indicating negligible biological breakdown during this period. Untreated crumbs slaked down in a few minutes under the same conditions. Treatments with 1 per cent sodium alginate protected the crumb structure for about 2 weeks, and 1 per cent of a dried compost conferred a low order of crumb stability which lasted for approximately 1 month. Greenhouse and outdoor plots tested periodically for aggregation during 2 years indicated that the stability to bacterial attack of CRD-189 is comparable to that of CRD-186.

Leaching. An experiment in which 40 gm. of treated soil crumbs were leached for 6 weeks with 8 to 10 liters of fresh water a day showed that the amount of polyelectrolyte lost was negligible, since the crumbs did not break down.

Mechanical loss of tilth. A third way in which aggregate stability might be reduced from the original high level produced by treatment is by mechanical breakdown. Greenhouse and field plots subjected to normal tillage practice and weathering for 2 to 3 years have not shown serious losses in degree of aggregation. As in natural soils of good structure (24), however, it was found that overtilage and compaction of the soil when either too wet or too dry could destroy the tilth.

Heavy working of treated soil in the laboratory at moisture levels above the lower plastic limit produced large and compacted water-stable clods. When a treated soil (76 per cent aggregation), allowed to dry and pulverized mechanically to pass a 0.25-mm. sieve, was moistened and reworked at an optimum water content the aggregation level had dropped to 21 per cent. Repetition of this cycle for a second time further reduced aggregation to 16 per cent. When sufficient ammonium hydroxide was added to raise the pH to 10.5 in remoistening the pulverized soil, this soil reformed crumbs having an aggregation level of 89 per cent. Similar reactivation could be accomplished by use of sodium hydroxide or by compounds providing phosphate ions.

In this loss of aggregation by drying and pulverizing, the binding effect was largely destroyed even though the polymer was still present and adsorbed on the soil particles. Presumably, the hydroxyl and phosphate ions desorbed the polymer and allowed it to be redistributed and readsorbed when the ultimate soil particles were again in an optimum random configuration. The soil did not become sticky or lose its good working properties after being broken down mechanically. This indicated that the workability factor is related to small unaggregated primary particles rather than to large aggregates.

Miscellaneous effects

One important point to be determined was the effect of aggregate-cementing materials on plant and animal life in the soil. The Warburg evaluation indicated that these polyelectrolytes were not toxic to yeast or to natural organisms present in the soil. Preliminary studies on rate of nitrification in a soil perfusion apparatus (1) indicated no detrimental effect upon organisms responsible for this function in soil. Spectroscopic analysis of kidney beans, wheat, and radish plants grown in treated and control soils indicated that nutrients and trace elements were not rendered unavailable in any way. This was borne out by the plant growth itself. Nor were the polymers found to be detrimental to earthworms in soil. In fact, the worms seemed to appear in even greater numbers in the friable and well-aerated soil which resulted from treatment with soil conditioners. That these polyelectrolytes had low acute toxicity to higher animals was shown by feeding CRD-186 and CRD-189 to rats and chickens in relatively large dosages with no ill effects.

Plant response

The soil conditioners have been subjected to greenhouse and field plot tests for more than 2 years. Plant responses obviously depend upon many factors,

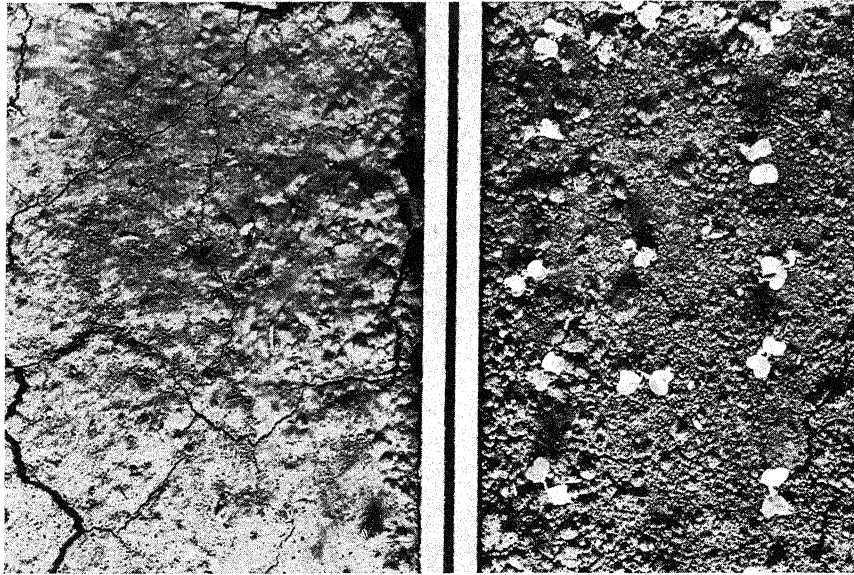


FIG. 3. EFFECT OF CRD-189 TREATMENT ON EMERGENCE OF RADISH SEEDLINGS

Greenhouse flats of Miami silt loam, left, untreated; right, treated with 0.05 per cent CRD-189. Treated soil showed no slaking, shrinkage, or crack formation.



FIG. 4. POINSETTIAS AT INCEPTION OF BLOOMING IN MIAMI SILT LOAM

Left: untreated; right: treated with 0.05 per cent CRD-189. Blooms of plants in conditioned soil later averaged twice the diameter of those in untreated soil.

including temperature, light, moisture, aeration, nutrient supply, plant diseases, and insects. Changing the structure of the soil may cause interrelated changes in a number of these factors. It is therefore difficult to determine the exact manner in which soil treatment affects plant growth.

One effect noted in most growing experiments was an increase in percentage of seed germination and in emergence of seedlings from treated soil (fig. 3). For example, the average germination of nine successive crops of radishes in pots of untreated Miami silt loam was 68 per cent, whereas the same soil treated with 0.02 per cent CRD-186 and 0.1 per cent CRD-186 allowed 77 and 82 per cent germination, respectively. Even greater differences were noted with sensitive crops like carrots. In one experiment with Miami silt loam in a greenhouse bench, only 32 per cent of the carrots emerged in the control, whereas the soil treated with 0.05 per cent CRD-186 allowed 63 per cent emergence. The reduction of crusting by treatment with polyelectrolytes virtually eliminated "neck-breaking" of radishes, beans, and other plants as they emerged.

Treatment of soil with polyelectrolytes resulted in faster plant growth, in earlier maturity, and usually in increased yields (fig. 4). A consistent benefit from soil treatment was increased root growth. This may be attributed largely

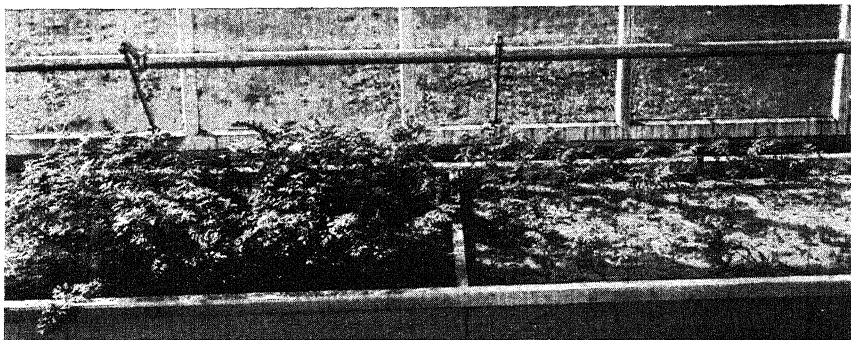


FIG. 5. CARROTS AFTER 3 MONTHS IN MIAMI SILT LOAM
Left, treated with 0.05 per cent CRD-186; right, untreated.

to increased availability of water and air, since Bayer (2) concluded that lack of sufficient water and air were the factors usually responsible for limiting root growth. Improved friability and porosity were also undoubtedly important factors.

Faster plant growth in treated soil is illustrated in figure 5, which shows carrots growing in treated and untreated soil. Since emergence had previously been poor in the control plot, several carrot seeds were planted in each spot to produce equal numbers of plants. At harvest, the carrots in the treated plot averaged 2.8 times the weight of the controls and were markedly improved in appearance (fig. 6).

CRD-189 at 0.05 per cent dosage was compared with a number of organic fertilizers at 1 per cent in flats of Miami silt loam in which 72 seeds were planted. The results are shown in table 7. CRD-189 alone gave an increase in average radish weight, and in combination with fertilizer, a still larger increase. The only organic fertilizer that produced a sizable weight increase was rotted cow manure. Sodium alginate added at 1 per cent induced severe denitrification, and the plants

were dwarfed and yellow. Addition of fertilizer with the sodium alginate gave excellent growth, in accordance with the findings of Owen (22).

The effect of polyelectrolytes upon aggregation of soils depends in large measure upon the rate at which the materials are added. Many investigators have



FIG. 6. CARROTS FROM TWO RATES OF TREATMENT IN TRIPLICATE 7-INCH POTS AFTER 3 MONTHS' GROWTH IN MIAMI SILT LOAM

Left, untreated, weight 7 gm.; center, treated with 0.02 per cent CRD-186, weight 35 gm.; right, treated with 0.1 per cent CRD-186, weight 56 gm.

TABLE 7

Effect of CRD-189 and organic fertilizers on growth of radishes in Miami silt loam

TREATMENT	DOSAGE	GERMINATION	AVERAGE RADISH WEIGHT FACTOR
	%	%	
None.....	—	86	1.0
CRD-189.....	0.05	85	1.7
CRD-189 + fertilizer*.....	0.05	78	3.4
Sodium alginate.....	1.0	71	0.04
Sodium alginate + fertilizer*.....	1.0	83	2.6
Commercial compost.....	1.0	83	1.1
Activated sewage sludge.....	1.0	49	0.64
Rotted cow manure.....	1.0	61	2.3
Peat.....	1.0	83	1.1

* 0.1 per cent of 6-10-4 by weight of soil (approximately 1,000 lb./A.)

concluded that the distribution of soil crumb sizes for optimum growth of plants lies in the range of 1-5 mm. As noted in table 4, increasing the rate of treatment gave larger and larger aggregates. In a greenhouse experiment, the average weights of radishes grown in Paulding clay soil treated with 0.02, 0.05, 0.1, and 0.5 per cent CRD-186 were 1.9, 1.7, 1.9, 0.9 times, respectively, that of the con-

trols. The high percentage of large aggregates obtained with the 0.5 per cent treatment might account for poor response at high dosage levels.

SUMMARY

Synthetic water-soluble polyelectrolytes have been synthesized which are extremely effective aggregate-cementing agents. When a polyanion, such as a hydrolyzed polyacrylonitrile, is applied at rates of 0.01 to 0.1 per cent to soil of poor structure, the aggregate analysis as determined by wet-sieving is increased, the working properties are improved, and other characteristics commonly associated with good structure are developed.

The treatment increases infiltration and percolation of water and thus reduces runoff. The moisture equivalent of the soil is increased, the wilting point being unchanged, so that the soil holds more water available for plant growth and the rate of evaporation from the soil surface is reduced. Because of the increase in water-stable aggregates, aeration in the treated soil is improved, and faster and more complete germination of seeds has been noted. Reduced crusting has resulted in easier seedling emergence. Faster plant growth and earlier maturity of plants in treated soil have been found. Significant yield increases of radishes, carrots, and other crops have been obtained in treated soil.

Treatments have remained effective for more than 2½ years. An effective experimental method is now available for quickly improving the structure of soils without affecting the nutrient status. These synthetic polyelectrolytes are believed to function as soil-cementing agents in the same manner as naturally occurring polyuronides. In addition, they are many times more active and resist bacterial decomposition for a much longer period.

REFERENCES

- (1) AUDUS, L. J. 1946 A new soil perfusion apparatus. *Nature* 158: 419.
- (2) BAVER, L. D. 1951 Effect of physical properties of soil on the efficient use of fertilizers. *Agron. Jour.* 43: 359-363.
- (3) BOUYOUCOS, G. J. 1935 Comparison between the suction method and the centrifuge method for determining the moisture equivalent of soils. *Soil Sci.* 40: 165-171.
- (4) BREAZEALE, J. F., AND McGEORGE, W. T. 1949 New technique for determining wilting percentage of soil. *Soil Sci.* 68: 371-374.
- (5) DUTT, A. K. 1948 Effect of water-soluble potassium silicate and various other treatments on soil structure and crop growth. *Soil Sci. Soc. Amer. Proc.* (1947) 12: 497-501.
- (6) ELLINGER, G., AND QUASTEL, J. H. 1948 Preliminary experiments in the study of the respiratory activity of microorganisms suspended in thin films of fluid adhering to solid surfaces. *Biochem. Jour.* 42: 214-218.
- (7) ESER, C. 1884 Untersuchungen über den Einfluss der physikalischen und chemischen Eigenschaften des Bodens auf dessen Verdunstungsvermögen. *Forsch. Gebeite Agr.-Phys.* 7: 1-124.
- (8) FELBER, I. M. 1944 Persistence of the moisture conserving effect of methyl cellulose in soil. *Amer. Soc. Hort. Sci. Proc.* 45: 331-337.
- (9) FEUSTEL, I. C., AND BYERS, H. G. 1936 Comparative moisture absorbing and moisture retaining capacities of peat and soil mixtures. U. S. Dept. Agr. Tech. Bul. 532.

- (10) FORSYTH, W. G. C., AND WEBLEY, D. M. 1949 Synthesis of polysaccharides by bacteria isolated from soil. *Jour. Gen. Microbiol.* 3: 395-399.
- (11) FULLER, W. H. 1947 Evidence of the microbial origin of uronides in soil. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 280-283.
- (12) GEOGHEGAN, M. J., AND BRIAN, R. C. 1948 Aggregate formation in soil. *Biochem. Jour.* 43: 5-13, 14.
- (13) GEOGHEGAN, M. J. 1950 Influence of some microbial metabolic products and other substances on aggregation of soil particles. *Fourth Internat. Cong. Soil Sci. Trans.* 1: 198-201.
- (14) LAWS, W. D., AND PAGE, J. B. 1946 Silicate of soda as a soil aggregating agent. *Jour. Amer. Soc. Agron.* 38: 95-97.
- (15) LAWS, W. D. 1951 Water-soluble silicate application to a calcareous clay soil and effect on soil properties and nutrient uptake by plants. *Soil Sci. Soc. Amer. Proc.* (1950) 15: 89-92.
- (16) LEES, H., AND QUASTEL, J. H. 1944 New technique for the study of soil sterilization. *Chem. and Indus.* 63: 238-239.
- (17) MCCALLA, T. M. 1945 Influence of microorganisms and some organic substances on soil structure. *Soil Sci.* 59: 287-297.
- (18) MARTIN, J. P., AND WAKSMAN, S. A. 1941 Influence of microorganisms on soil aggregation and erosion. *Soil Sci.* 52: 381-394.
- (19) MARTIN, J. P. 1943 Effect of compost and compost materials upon the aggregation of the silt and clay particles of Collington sandy loam. *Soil Sci. Soc. Amer. Proc.* (1942) 7: 218-222.
- (20) MARTIN, J. P. 1945, 1946 Microorganisms and soil aggregation. *Soil Sci.* 59: 163-174 (1945); 61: 157-166 (1946).
- (21) NORMAN, A. G., AND BARTHOLEMW, W. V. 1943 Chemistry of soil organic matter. *Soil Sci.* 56: 143-150.
- (22) OWEN, O. 1949 Use of alginates as a source of organic carbon in soil. *Cheshunt Exp. Res. Sta. Rpt.* 1948: 70-72.
- (23) QUASTEL, J. H., AND WEBLEY, D. M. 1947 Effects of the addition to soil of alginic acid and of other forms of organic matter on soil aeration. *Jour. Agr. Sci.* 37: 257-266.
- (24) RUSSELL, E. W. 1938 Soil structure. Imp. Bur. Soil Sci. Tech. Commun. 37.
- (25) SHOREY, E. C., AND MARTIN, J. B. 1930 Presence of uronic acids in soils. *Jour. Amer. Chem. Soc.* 52: 4907-4915.
- (26) SWABY, R. J. 1950 Influence of humus on soil aggregation. *Jour. Soil Sci.* 1: 182-194.
- (27) VAN BAVEL, C. M. H. 1950 Use of volatile silicones to increase water-stability of soil. *Soil Sci.* 70: 291-297.
- (28) WEBLEY, D. M. 1947 Technique for the study of oxygen availability to microorganisms in soil and its possible use as index of soil aeration. *Jour. Agr. Sci.* 37: 249-256.
- (29) WINTERKORN, H. F., FEHRMAN, R. G., AND MCALPIN, G. W. 1946 Waterproofing cohesive soils by resinous treatment. *Soil Sci. Soc. Amer. Proc.* (1945) 10: 450-460.
- (30) YODER, R. 1936 Direct method of aggregate analysis of soils and a study of the physical nature of erosion losses. *Jour. Amer. Soc. Agron.* 28: 337-351.

EFFECT OF SYNTHETIC POLYELECTROLYTES ON THE STRUCTURE OF SALINE AND ALKALI SOILS

L. E. ALLISON

U. S. Department of Agriculture¹

Soils that are affected with salt commonly occur in regions of arid or semiarid climate. Such soils are conveniently divided into three classes: saline, saline-alkali, and nonsaline-alkali (11), all of which present problems of plant growth. Saline soils contain an appreciable quantity of soluble salts; and alkali soils, whether saline or nonsaline, are characterized chiefly by a high content of exchangeable sodium in the cation-exchange complex.

Plant growth is adversely affected on saline soils as a consequence of the increase in osmotic pressure and the accompanying decrease in the physiological availability of water which result from an accumulation of neutral salts in the soil solution. In addition, growth may be restricted through the accumulation of toxic quantities of various ions within the plant (5, 6, 9). Plant growth on alkali soils may be depressed because of the low availability of calcium and magnesium (2, 7). More often, however, low productivity on these soils is believed to result primarily from unfavorable physical conditions induced by their high content of exchangeable sodium. Reviews of plant growth on saline and alkali soils have been published by Magistad (9) and Hayward and Wadleigh (6).

Recent studies have indicated that when sodium comprises more than 10 or 15 per cent of the total exchangeable cations, the soil tends to become dispersed (3, 9). When irrigated and cultivated in this condition, the soil disaggregates or loses its favorable structure and becomes relatively impermeable to water and air. Under these conditions infiltration of irrigation water is retarded and internal drainage is restricted. McGeorge and Breazeale (8) presented evidence that plant growth is restricted on puddled or dispersed soils by a combination of factors involving nutrient availability, lowered water availability, and poor gaseous interchange which, because of low oxygen tensions, may further limit the uptake of water by roots.

Fireman and Reeve (4) studied the factors responsible for the high incidence of barren spots in an alkali soil area in Idaho and found that poor infiltration in the barren areas caused the soil to be deficient in moisture most of the time. In these spots the amount of soluble salt in the soil was low, but the proportion of exchangeable sodium on the exchange complex was high. Thus the poor structural condition of the soil resulting from a high-sodium condition prevented adequate replenishment of soil moisture, which is essential for plant growth.

Where high-sodium conditions exist, it is considered necessary to replace the excess adsorbed sodium and leach it from the rhizosphere before soil structure can be improved. In some cases, leaching without added amendments may attain this objective, especially if calcium and magnesium are available in the

¹ Contribution from the U. S. Salinity Laboratory, Riverside, California, in cooperation with the seventeen Western States and the Territory of Hawaii.

irrigation water or if gypsum is present in the soil. More often it is necessary to supply soluble calcium to replace the adsorbed sodium. This is done either by applying gypsum or, if the soil is calcareous, by bringing calcium into solution by applying acid or acid-forming materials. With any of these soil improvement treatments, however, considerable time may be required for the soil to attain good structure through natural processes, and during this time economic returns may be low. In view of these facts, it is evident that a need exists for a method of treating dispersed soils which will rapidly restore good soil structure. Even though such a treatment might be somewhat expensive, it may be economically feasible, provided immediate profitable crop yields are obtained.

This paper presents the results of a preliminary laboratory and field study of the effect of two commercial soil conditioners in promoting water-stable aggregation in western soils. The products² under study are synthetic polyelectrolytes: CRD-186 is a calcium carboxylate polymer, and CRD-189 the sodium salt of a hydrolyzed polyacrylonitrile (Krilium). In this preliminary study, no attempt was made to simulate economic field practice. Rather, it was decided to use these materials as a research tool to distinguish between the chemical and the physical or structural factors affecting plant growth on saline and alkali soils. As hereafter used in this report, the term "treatment" refers specifically to the application of these materials.

LABORATORY STUDIES

A preliminary laboratory study was made to determine the ability of CRD-186 to produce water-stable aggregation and its effect on permeability. For this purpose, samples of the local Pachappa fine sandy loam and the A and B horizons of Sebree soil were used. The latter is an alkali, or "slick" spot soil from the Black Canyon Project, Idaho, which occurs on many thousands of acres of problem land in that area.

The polyelectrolyte conditioners were applied in a water solution by directing a fine spray into dry soil. In some cases the soil was finely ground, and in others it was passed through a $\frac{1}{8}$ -inch sieve. Unless otherwise stated, 1,000-gm. lots of soil were treated with the conditioners at rates of 0.025 and 0.100 per cent by weight on a dry basis and the amount of water applied was sufficient to wet each soil to at least three-fourths field capacity. Care was used in manipulation to produce as little physical change as possible during treatment. For the initial experiment reported in table 1, the soils were treated in a metal beaker, mounted on a revolving wheel set at a 45° angle. Thereafter, the treatments were made on a rubberized mixing cloth, with frequent rolling of the sample to avoid local overwetting. The control samples were similarly treated with water and otherwise received the same mechanical working. All treated samples were held overnight in a moist condition and then were passed through a 4-mm. sieve and air-dried for analysis.

Aggregate analyses were made by a modification of the Yoder wet-sieving procedure (10) using 60-gm. samples, a $1\frac{1}{2}$ -inch stroke at 30 cycles per minute,

² Products supplied by Monsanto Chemical Company.

a washing period of 30 minutes, and five sieves having openings of 2, 1, 0.5, 0.25 and 0.10 mm. Water permeability was determined with the apparatus described by Bower and Peterson (1). Chemical analyses were made according to the methods used at this laboratory (11).

The data in table 1 indicate that CRD-186 effectively aggregated the Pachappa soil and the Sebree subsoil, but that it was much less effective on the Sebree topsoil. Since the latter soil contains less than 3 per cent of 2μ clay (table 2)

TABLE 1

Effect of CRD-186 treatment on aggregation and permeability of three soils of widely varying characteristics

SOIL	TREATMENT AS PER CENT OF SOIL	SALINITY ($EC_e \times 10^3$)*	EXCHANGE- ABLE SODIUM	WATER- STABLE AG- GREGATES <0.10 mm.	PERMEABILITY 6 INCHES WATER APPLIED	
					1st inch	6th inch
Pachappa fine sandy loam†	None	<1	0	%	cm./hr.	cm./hr.
	.025			18	3.3	3.1
	.100			46	4.9	5.1
		<1	30	61	3.1	3.1
	None			22	3.2	1.8
	.025			56	3.8	3.9
	.100			67	5.4	5.3
	None	<1	75	24	1.9	1.2
	.025			69	5.4	5.3
	.100			74	4.4	4.3
Sebree silt loam (0-5 inches)	None	1	13	27	0.64	0.40
	.025			28	0.74	0.38
	.100			39	0.98	0.33
Sebree clay loam (5-12 inches)	None	2.5	34	21	1.6	0.4
	.025			37	4.8	3.7
	.100			80	6.7	5.0

* Expressed as electrical conductivity of saturated soil extract in millimhos per centimeter at 25°C. (11).

† This Pachappa soil was prepared by C. A. Bower for another experiment requiring different levels of exchangeable sodium. Since the permeabilities of these manipulated samples are considerably higher than those for field soils having similar sodium levels, these data must be interpreted in the light of this fact.

and otherwise is chiefly silt and fine sand, it would not be expected to adsorb the conditioner and produce so high a degree of aggregation as soils having considerably higher clay content. Based on the differences obtained with these soils, it appears that the amount of clay in the soil is a dominant factor in determining the aggregating efficiency of polyelectrolyte soil conditioners such as CRD-186. Elsewhere in this issue, Ruehrwein and Ward discuss the reaction between synthetic polyelectrolytes and clay which governs formation of water-stable aggregates.

TABLE 2
Comparison of the aggregating effectiveness of CRD-186 and CRD-189 on nonsaline and alkali soils

SOIL NO.	SOIL TYPE	SOIL CHARACTERISTICS					WATER-STABLE AGGREGATES			
		pH*	Salinity ($EC_e \times 10^3$)*	Exch. sodium	Clay (2μ)	Treat- ment as per cent of soil	CRD-186		CRD-189	
							<0.25 mm.	<0.10 mm.	<0.25 mm.	<0.10 mm.
Nonsaline soils										
2648B	Pachappa fine sandy loam	7.7	0.7	Nil	13	None	7	14	—	—
						.025	45	58	30	44
						.100	69	81	59	71
2737	Sebree silt loam (0-5 inches)	6.5	1.0	13	3	None	6	20	—	—
						.025	20	28	18	23
						.100	27	39	44	57
2741	Chilcott silt loam†	6.4	0.6	Nil	16	None	12	18	—	—
						.025	—	—	—	—
						.100	80	89	64	77
3278	Las Flores clay loam	8.2	2.1	14	31	None	14	25	—	—
						.025	24	41	35	51
						.100	57	69	68	77
Alkali soils										
2738	Sebree clay loam (5-12 inches)	7.3	2.5	34	24	None	9	18	—	—
						.025	20	37	30	47
						.100	58	80	64	73
3276	Chino silty clay	10.0	16	92	41	None	3	9	—	—
						.025	33	48	25	37
						.100	62	72	60	70
3277	Chino clay	8.4	36	73	56	None	2	4	—	—
						.025	20	28	22	31
						.100	40	47	44	49
2763	Umapine silt loam†	8.1	4.5	26	18	None	16	38	—	—
						.025	—	—	—	—
						.100	72	85	74	88
57	Imperial clay (6-18 inches) gypsiferoust†	7.2	48	—	70	None	12	25	—	—
						.025	—	—	—	—
						.100	56	64	24	31

* pH was determined on a saturated soil paste, and salinity was determined on the extract therefrom and expressed as electrical conductivity in millimhos per centimeter at 25°C. (11).

† These three soils were passed through a $\frac{1}{8}$ -inch sieve and all others were finely ground prior to treatment.

As determined by permeability measurements, the CRD-186 treatment, at both the 0.025 and 0.100 per cent levels, exhibited a pronounced tendency to overcome the dispersive effect of a high content of exchangeable sodium. Permeability was as high for the Pachappa soil and nearly as high for the Sebree sub-

soil at the end of the test (after 6 inches of water had passed the soil column) as it was after passage of the first inch of water. The treated Seabee topsoil exhibited the least tendency to overcome sodium dispersion, probably because of its deficiency of clay.

A comparison of the aggregating effectiveness of CRD-186 and CRD-189 on nine western soils which vary widely in several chemical and physical characteristics is presented in table 2. Regardless of pH, salinity, percentage of exchangeable sodium, or clay content of the various soils tested, there appears to be no significant difference in the ability of these two polyelectrolyte conditioners to produce water-stable aggregates for all except one of these soils. Imperial clay gave high aggregation with CRD-186 but relatively less aggregation with CRD-189. This is a subsoil (6-18-inch) from the Imperial Valley, California, and contains considerable gypsum, which may account for this anomalous behavior.

FIELD STUDIES

A field study of the effect of soil conditioner CRD-186 on aggregation and on crop growth was conducted during the summer of 1951 on Pachappa fine sandy loam soil with sweet corn as the test crop. This is a normal soil but it tends to form a surface crust on drying, and in this respect it is characteristic of many western alkali soils. The crusted condition that develops is a serious hazard to seedling emergence and the establishment of a stand of many crops, such as beans and sugar beets.

The four plots (10 feet by 10 feet) used for this study were from a previous experiment conducted in 1949. These plots were idle during 1950. As a consequence of the treatments used in the previous experiment, the following soil conditions resulted, which were well suited for this experiment; namely, normal soil, nonsaline-alkali soil, and saline-alkali soil, the last at two levels of salinity. The pH, salinity, and percentage of exchangeable sodium of the soil in these plots just prior to treatment with CRD-186 are shown in table 3. In general, the chemistry of the subsoil (6-18 inch) was similar to that of the surface soil, with the exception of plot 3, where the subsoil salinity was approximately half that of the surface soil.

For this experiment the original 10-foot by 10-foot areas, representing the four soil conditions mentioned, were subdivided into two 5-foot by 5-foot plots each (fig. 1). One plot of each pair was treated with 0.1 per cent CRD-186 on the dry basis to a depth of 6 inches and the other plot served as a control or check plot. The conditioner (1044 gm. dissolved in 125 liters of irrigation water) was sprayed on the soil and incorporated to a depth of 6 inches, the two operations taking place concurrently. The rotary cultivator used was a small motor-driven machine with a long-toothed rotor approximately 1 foot in diameter and 2 feet long. The depth of cultivation and rate of rotation were readily controllable, the latter being between 80 and 100 rpm. Sufficient water containing the conditioner was applied to bring the nearly dry field soil to about 13 per cent moisture, or three-fourths field capacity. An equal amount of water was applied to each control plot so that both treated and untreated plots received the same amount of wetting

and mechanical mixing. Immediately after the conditioning treatments the soil was tamped down slightly.

The conditioning treatments were made June 12-15, but because of the prevalence of foggy mornings, planting was delayed until weather conditions were more favorable for surface crusting. All plots were preirrigated on July 11 with 2.5 inches of water. The surface condition of the CRD-186-treated and untreated

TABLE 3

Salinity and alkali condition of Pachappa fine sandy loam plots prior to treatment with 0.1 per cent CRD-186, and effect of treatment on aggregation and infiltration rates

Plot No.		1	2	3	4				
Soil condition		Normal soil	Nonsaline-alkali	Saline-alkali No. 1	Saline-alkali No. 2				
<i>Chemical characteristics</i>									
	<i>Depth (in.)</i>								
pH	0- 6	7.8	8.3	8.0	7.7				
	6-18	7.6	8.2	7.9	7.4				
Salinity ($EC_e \times 10^3$)	0- 6	0.8	3.0	23.3	12.7				
	6-18	0.9	1.6	11.8	10.1				
Exchangeable sodium per-centage	0- 6	3	29	47	40				
	6-18	3	25	48	42				
<i>Percentage water-stable aggregates</i>									
Aggregate class		<0.25 mm.	<0.10 mm.	<0.25 mm.	<0.10 mm.	<0.25 mm.	<0.10 mm.	<0.25 mm.	<0.10 mm.
Treated.		53	69	69	84	70	83	67	84
Untreated.		24*	31*	25*	31*	25*	30*	25*	31*
<i>Infiltration rates (in./hr.)</i>									
		1st Irrigation— (2.5 in. of water applied)							
Treated.		6.2	6.2	6.2				5.6	
Untreated.		5.4	1.3			.16		.35	
		8th Irrigation— (2 to 3 in. of water applied)							
Treated.		6.0	4.0			.53		.50	
Untreated.		3.3	.18			.05		.06	

* Chiefly primary particles, including stones 2 to 4 mm. in size.

plots 2 days after irrigation is shown in figure 1. Golden Cross Bantam sweet corn (T-strain) was planted on July 19 at the rate of 20 hills per plot and three kernels per hill. Later it was thinned to two plants per hill. Immediately after planting, a 1.5-inch irrigation was applied. Nitrogen was supplied by adding ammonium and potassium nitrates to the irrigation water as needed. Superphosphate was applied at the rate of 1,000 pounds per acre prior to the conditioning treatment. A total of 21 inches of Riverside irrigation water was applied

during the experiment. This water is of good quality, the conductivity being 360 micromhos per cubic centimeter, with sodium comprising 40 per cent of the total cation content when expressed on a chemical equivalent basis.

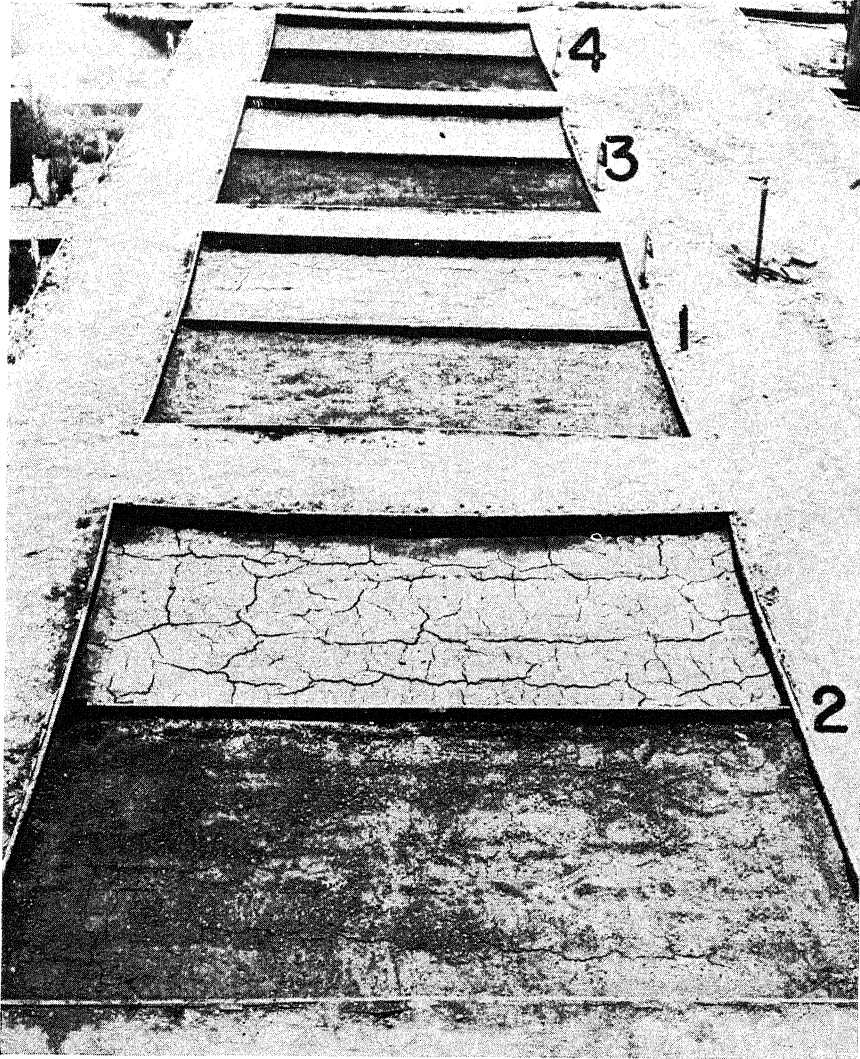


FIG. 1. VIEW OF PLOTS 2 DAYS AFTER INITIAL IRRIGATION WITH 2.5 INCHES OF WATER, SHOWING CRACKED AND CRUSTED CONDITION OF UNTREATED ALKALI SOIL IN PLOTS 2, 3, AND 4

Treated plots are in the foreground in each case.

To determine the effect of treatment on the production of water-stable aggregates, samples from the 0-6-inch layer were taken 1 day after treatment. They were passed through a 4-mm. screen, air-dried, and wet-sieved. The data

in table 3 indicate that a high degree of water-stable aggregation was attained by the 0.1 per cent CRD-186 treatment regardless of the chemical status of the soil. Pachappa fine sandy loam is virtually devoid of natural aggregates but contains stone fragments; consequently, the material remaining on the sieves from the untreated plots was almost entirely primary particles. The wet-sieved fractions of the treated samples showed little or no evidence of free stones, indicating that the conditioner effectively binds together into water-stable aggregates small stones between 2 and 4 mm. and soil particles less than 2 mm. Aggregation due to treatment was as high on the two saline-alkali soils as on the nonsaline-alkali soil (plots 3 and 4 *vs.* 2), indicating that salinity *per se* did not inhibit the aggregation process. Moreover, aggregation was significantly higher on all of the alkali soils than on the normal soil (plots 2, 3, and 4 *vs.* 1). This phenomenon was also observed (table 1) for the same Pachappa soil studied in a previous laboratory experiment. Though a high sodium content apparently favors high aggregation in soils treated with conditioner CRD-186, the present evidence is too limited to serve as a basis for final conclusion on this point.

Measurements of infiltration rate were made at the first and eighth irrigations (table 3). The normal Pachappa soil is highly permeable, and for that reason the treatment with CRD-186 gave only a very slight increase in infiltration rate on this soil. Its effect, however, in improving the infiltration rate of the soil in the alkali plots (plots 2, 3, and 4) is striking. The infiltration rates on all three alkali soils tended to decrease with successive irrigations but, despite this fact, the improvement associated with the treatment was always appreciable.

Observations during the course of this experiment indicated that after each irrigation the untreated alkali plots dried out rapidly, forming a crust 1 inch or more thick; whereas the treated soils were loose and appeared fairly moist throughout most of the interval between irrigations. Since the CRD-186 treatment greatly increased infiltration rates on these plots (table 3), it might also be expected to facilitate upward rise of moisture into the treated surface from the untreated soil below. Capillary rise was measured at the end of the experiment on 0-6-inch samples from all plots (fig. 2). From the relative position of the curves, it is evident that treatment with CRD-186 gives the alkali soils in plots 2, 3, and 4 moisture transmission characteristics, within the zone of treatment, similar to those of the normal soil of plot 1.

The data for stand and yields are shown in table 4 and illustrated in figures 3, 4, and 5. Full stands of sweet corn were obtained on all CRD-186-treated soils and on the untreated normal soil, but, stands on the untreated alkali plots varied from 0 to 5 very weak hills per plot, some of which contained only one stalk. Most of the plant emergence on the untreated alkali plots was through cracks produced in the surface crust (fig. 1). Quality of the corn was excellent, and yields were considered good despite the prevailing high temperatures. During the first 40 days of this experiment, beginning on July 19, maximum daily temperatures ranged from 86 to 102°F. with only 8 day below 90, and during mid-September, when ears were maturing, daily maximum temperatures ranged from 100 to 106° for a 5-day period.

The most striking feature of this experiment is the higher yield, 4,046 gm., of corn on the treated nonsaline-alkali soil as compared to a yield of 3,822 gm. on

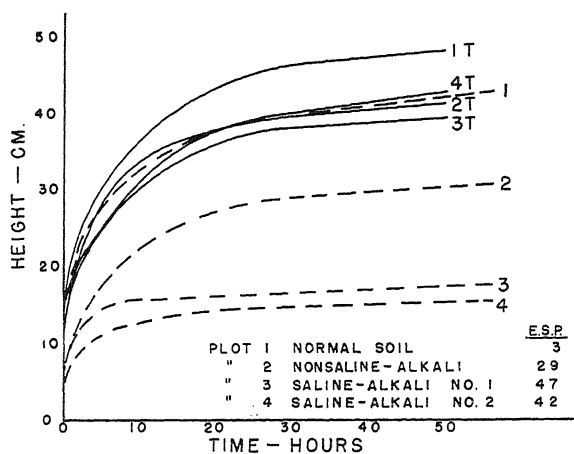


FIG. 2. EFFECT OF 0.1 PER CENT CRD-186 TREATMENT (T) ON THE CAPILLARY RISE OF MOISTURE IN PACHAPPA FINE SANDY LOAM FROM FIELD PLOTS

TABLE 4

Effect of soil treatment with 0.1 per cent CRD-186 on stand, height, and yield of sweet corn

Plot Number	1	2	3	4
Soil Condition	Normal soil	Nonsaline-alkali	Saline-alkali No. 1	Saline-alkali No. 2
<i>Per cent stand</i>				
Treated	100	100	100	100
Untreated	100	30	0	40
<i>Average height—inches</i>				
Treated	60	60	49	51
Untreated	54	43	0	30
<i>Number of ears and average weight per ear—gm.</i>				
Treated	28-137	26-156	21-105	17-118
Untreated	26-142	5-151	0- 0	0- 0
<i>Total yield—gm.</i>				
Treated	3822	4046	2208	2003
Untreated	3701	756	0	0

the treated normal soil. Though the statistical significance of this difference may be questioned, it indicates that for this crop and under the conditions of this



FIG. 3. SWEET CORN ON TREATED AND UNTREATED NORMAL PACHAPPA SOIL—PLOT 1

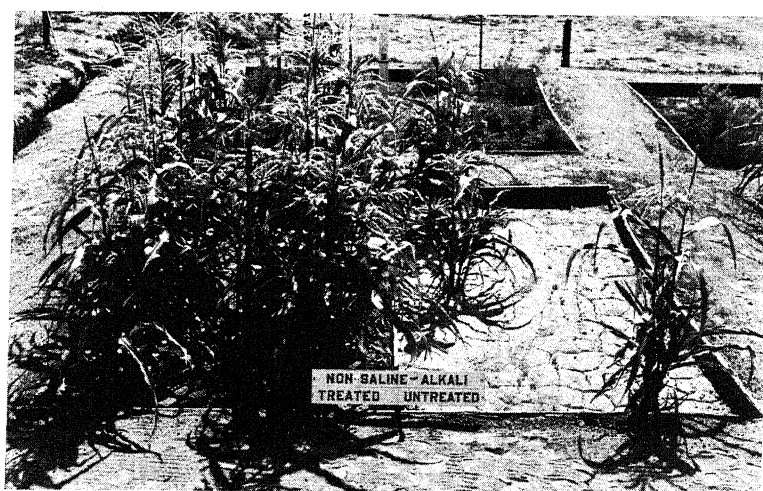


FIG. 4. SWEET CORN ON TREATED AND UNTREATED NONSALINE-ALKALI PACHAPPA SOIL—PLOT 2

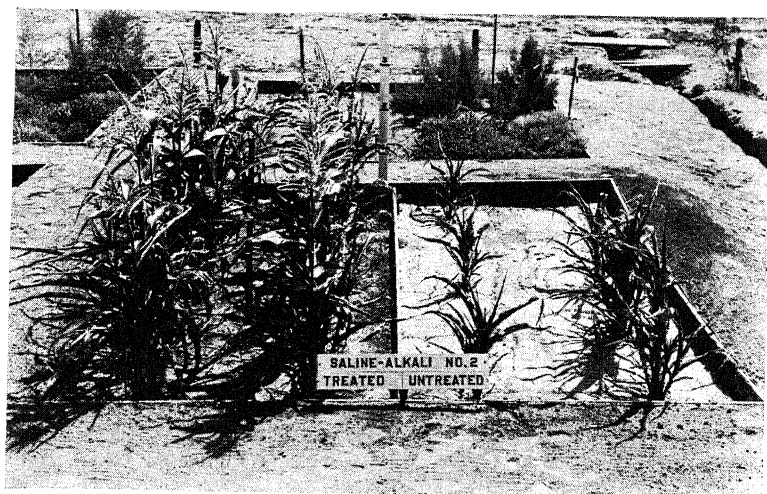


FIG. 5. SWEET CORN ON TREATED AND UNTREATED SALINE-ALKALI PACHAPPA SOIL NO. 2—PLOT 4

experiment the high-sodium condition (percentage exchangeable sodium = 29) was not *per se* a growth-inhibiting factor, provided the soil had good structure. It is not inferred, however, that this phenomenon would necessarily obtain for all crops or for different soils. Whereas the CRD-186 treatment did not significantly increase yields on the normal soil, it gave very large increases on all three alkali soils, primarily because of stand failure or poor growth of the few surviving plants on the untreated plots. Corn yields on the treated saline-alkali soils in plots 3 and 4 were approximately half those obtained on the treated nonsaline soils in plots 1 and 2 (table 4). These differences are attributed to the high salt content of the soil in these plots during the early part of the experiment, rather than to any differences in alkali conditions.

TABLE 5

*Effect of soil treatment with 0.1 per cent CRD-186 on removal of salt and exchangeable sodium from surface soil**

Plot No.	1	2	3	4
Soil condition	Normal soil	Nonsaline-alkali	Saline-alkali No. 1	Saline-alkali No. 2
<i>Salinity (millimhos/cm.)</i>				
Before experiment.....	.8	3.0	23.3	12.7
After—untreated plot.....	.8	1.8	7.1	5.0
After—treated plot.....	.7	1.1	1.8	1.5
<i>Exchangeable sodium (me./100 gm.)</i>				
Before experiment.....	.26	2.27	3.86	3.33
After—untreated plot.....	.03	1.23	3.79	2.69
After—treated plot.....	.04	1.03	2.94	1.98
<i>Percentage exchangeable sodium</i>				
Before experiment.....	3	29	47	40
After—untreated plot.....	<1	15	46	31
After—treated plot.....	<1	12	33	22

* Twenty-one inches of irrigation water were applied during this experiment.

The effect of irrigation with 21 inches of Riverside irrigation water upon the removal of salt and exchangeable sodium with corresponding change in percentage of exchangeable sodium is shown in table 5. Marked reductions in salinity and exchangeable sodium were obtained, the greatest changes occurring on the treated plots. These data suggest that the CRD-186 treatment, as used in this investigation, appeared to facilitate the reclamation process.

The extent to which soil conditioners may find use for physical improvement of alkali soils depends, aside from cost, upon the stability of the conditions against chemical and microbial decomposition. Since synthetic polyelectrolytes are organic in nature, it is thought that they are subject to some degree of microbial attack, with resulting loss of effectiveness in maintaining a high degree of water-stable aggregation. Experiments are in progress at the Salinity Laboratory on saline and alkali soils treated with CRD-186 to determine changes in water-stable aggregation with time. In addition, the plots described herein will be continued with other crops.

DISCUSSION AND SUMMARY

Laboratory tests were made on several saline and alkali soils from the Western States to determine the aggregating effectiveness of synthetic polyelectrolytes CRD-186 and CRD-189. In all cases, the conditioners were applied in solution at rates of 0.025 and 0.1 per cent by spraying the solution into dry soil, followed by mixing to facilitate aggregation. Aggregate analysis by wet-sieving indicates that these two soil conditioners are about equally effective in producing high water-stable aggregation. Tests made on alkali soils that were low in permeability and that were treated with CRD-186, as indicated, gave marked increases in permeability in proportion to rate of treatment.

Sweet corn was grown on treated and untreated field plots representing normal, nonsaline-alkali, and saline-alkali soil conditions, the last at two levels of salinity. The CRD-186 was applied in solution (spraying) at the rate of 0.1 per cent to a depth of 6 inches while the soil was being mixed with a small power-operated cultivator. This treatment gave many-fold increases in irrigation water infiltration on the alkali soils but had little or no effect on the normal soil.

Full stands of corn were obtained on all treated plots and on the untreated normal soil plot, but because of heavy crust formation, stands on the untreated alkali soil plots varied from 0 to 40 per cent with little or no yield. Quality of the corn produced was excellent, and the yields from the 20 hills on each treated plot and on the untreated normal soil were as follows: nonsaline-alkali soil, 4,046 gm.; normal soil, 3,822 gm.; normal soil (untreated), 3,701 gm.; saline-alkali soil No. 1, 2,208 gm.; and saline-alkali soil No. 2, 2,003 gm. Yield suppression on the last two plots is attributed to the high salinity present rather than to the alkali or high-sodium condition.

REFERENCES

- (1) BOWER, C. A., AND PETERSEN, R. K. 1950 Technic for determining the permeability of soil cores obtained with the Lutz sampler. *Agron. Jour.* 42: 55-56.
- (2) BOWER, C. A., AND TURK, L. M. 1946 Calcium and magnesium deficiencies in alkali soils. *Jour. Amer. Soc. Agron.* 38: 723-727.
- (3) FIREMAN, M., AND MAGISTAD, O. C. 1945 Permeability of five western soils as affected by the percentage of sodium of the irrigation water. *Amer. Geophys. Union Trans.* 26: 91-94.
- (4) FIREMAN, M., AND REEVE, R. C. 1949 Some characteristics of saline and alkali soils in Gem County, Idaho. *Soil Sci. Soc. Amer. Proc.* (1948) 13: 494-498.
- (5) HARRIS, F. S. 1915 Effect of alkali salts in soils on the germination and growth of crops. *Jour. Agr. Res.* 5: 1-53.
- (6) HAYWARD, H. E., AND WADLEIGH, C. H. 1949 Plant growth on saline and alkali soils. *Advances in Agron.* 1: 1-38.
- (7) KELLY, W. P. 1928 A general discussion of the chemical and physical properties of alkali soils. *First Internatl. Cong. Soil Sci. Proc.* 4: 483-489.
- (8) McGEORGE, W. T., AND BREAZEALE, J. F. 1938 Studies on soil structure: Effect of puddled soils on plant growth. *Ariz. Agr. Exp. Sta. Tech. Bul.* 72.
- (9) MAGISTAD, O. C. 1945 Plant growth relations on saline and alkali soils. *Bot. Rev.* 11: 181-230.
- (10) RUSSEL, M. B. 1949 Methods of measuring soil structure and aeration. *Soil Sci.* 68: 25-35.
- (11) U. S. Salinity Laboratory, L. A. RICHARDS, editor. 1947 Diagnosis and Improvement of Saline and Alkali Soils. Riverside, Calif.

SOIL AND CROP RESPONSES FROM FIELD APPLICATIONS OF SOIL CONDITIONERS

W. P. MARTIN, G. S. TAYLOR, J. C. ENGIBOUS, AND E. BURNETT

Ohio Agricultural Experiment Station¹

The purpose of this study was to investigate thoroughly the possibilities for structural improvement of soil by Krilium* soil conditioners (synthetic polyelectrolytes). Laboratory tests had shown that these compounds in quantities ranging from 0.02 to 0.2 per cent, by weight of dry soil, produced marked increases in soil aggregation and related properties, appeared to have no adverse influence on available moisture capacity of the soil, did not tie up plant nutrients, seemed to be highly resistant to microbial destruction, and were not likely to be leached out of the soil.

Field tests were consequently established on several soils. The objectives were to utilize, on several "problem" soils, different conditioners at various rates of application and with various methods of incorporation and to note not only resulting changes in the physical characteristics of the soils but also the effect on different crops. It was desired to find crops that would be particularly responsive to structural change in soil and that could subsequently be used as "indicator" plants. Vegetable crops like potatoes or carrots were utilized because both quality and yield are important factors in production. Small-seeded legumes, like alfalfa, were used because of emergence problems in crusted soils. The fixation of nitrogen by the root-nodule bacteria and thus the protein content of the plant may also be influenced by the structural condition of the soil.

Representative experiments are reported in this paper.

MATERIALS AND METHODS

The several soil conditioners used in these experiments are designated as CRD-186, CRD-189, C-I, C-II, and C-III. All are polyelectrolytes. CRD-189, for example, is made by the hydrolysis of polyacrylonitrile to what is predominantly a sodium salt of the polyacid. CRD-186 is another carboxylated polymer which has a higher tolerance for calcium ions and can be formulated as a partial calcium salt. All are hydrophylic and readily soluble in soil moisture. They are very fine, yellowish or grayish-white powders which take up moisture readily. If the conditioner becomes wetted prior to incorporation, mixing is rendered exceedingly difficult because of the gelatinous mass that is formed.

Field application of soil conditioners were generally made in spring at times when the soil surface was dry enough to prevent this "gumming up" effect prior

*Trade-mark of the Monsanto Chemical Company.

¹ Contribution from department of agronomy, Ohio State University and Ohio Agricultural Experiment Station. Journal Article No. 29-52. The authors express appreciation to G. W. Volk and J. L. Mortensen, for much help and criticism during the course of this investigation and writing of the manuscript. This work was supported in part by the Monsanto Chemical Company. Appreciation is expressed for this and also for the many courtesies extended the authors by the researchers of the Central Research Department, Dayton, Ohio.

to incorporation. Soil moisture contents below the surface were near field capacity. The powder was spread evenly over the soil surface with a lime or fertilizer spreader and then rapidly incorporated either with a disk or a rototiller to a depth of 4 to 6 inches. Double diskings or rototillings for thorough incorporation were generally practiced.

Thorough mixing of the conditioner and the soil is essential for maximum aggregation. With soil moisture near field capacity, changes in structural conditions are noticeable within an hour after incorporation. When the conditioners are applied to soil near the wilting percentage, no noticeable changes in aggregation are observed until wetted by irrigation or rainfall.

Surface applications were raked in lightly by hand. Ground preparation prior to application consisted of plowing and disking or "culti-mulching" in the usual manner for seedbed preparation. Plantings were made as soon after application as possible, and usually the same day.

Most of the experiments were conducted on the Ohio State University Farm or at outlying experimental fields of the Ohio Agricultural Experiment Station. All

TABLE 1
Some chemical properties of Crosby, Miami, Brookston, and Paulding soils

SOIL TYPE	pH VALUE	ORGANIC MATTER	EX- CHANGE- ABLE POTASSIUM	SOLUBLE PHOS- PHORUS	LIME RE- QUIREMENT
		<i>per cent</i>	<i>lb./A.</i>	<i>lb./A.</i>	<i>tons/A.</i>
Crosby silt loam.....	5.7	2.53	170	30	2.0
Miami silt loam.....	5.8	0.76	51	12	2.0
Brookston clay loam.....	6.9	2.93	1140	1200	0
Brookston silty clay loam.....	6.0	4.34	188	57	1.7
Paulding clay.....	6.4	3.70	170	142	0

were of accepted statistical design (5) with treatments applied within the several replications at random. So far as possible, fertility factors were eliminated with fertilizer and crops were irrigated with a sprinkler-type system. Plot sizes varied, only the center parts being harvested. Essential details of the individual experiments are given in tables 7 to 12.

Field work was established on Crosby and Miami silt loams, Brookston clay and silty clay loams, and Paulding clay. Profile descriptions have been given by Conrey *et al.* (6). Pertinent chemical data on these soils are given in table 1.

Textural classification was based on sand, silt, and clay fractionation by the Bouyoucos hydrometer method (2). The pH values were determined with the Beckman glass electrode, exchangeable potassium by the Bray method,² and soluble phosphorus by the Dickman-Bray procedure (7). Organic matter was determined by Bingeman's modification³ of a combination of McCready and Hassid (11) and Gortner's (8) methods.

² Bray, B. H. Photometer method for determining available potassium in soils. Univ. Ill. Agr. Exp. Sta. Mimeo. Pamphlet. 1945.

³ Bingeman, C. W. Determination of total carbon in soil and organic material. Ohio Agr. Exp. Sta. Mimeo. Pamphlet. 1951.

Soil samples were collected periodically from the different plots for physical analyses. Disturbed samples were collected with a shovel or soil tube to a depth of 6 inches from many locations in each plot. These were composited in the usual manner. Undisturbed samples were taken with a core sampler. Disturbed samples were analyzed for the percentage of water-stable aggregates, and undisturbed soil cores for porosity and permeability by procedures outlined in the following section.

RESULTS AND DISCUSSION

Effect on physical properties of soils

Addition of soil conditioners in small amounts has produced measurable changes in the physical properties of several soils in Ohio. There is conclusive evidence of an increase in water-stable aggregates in treated soil. As a consequence of greater aggregation, changes in pore-size distribution, water infiltration, saturated water permeability, and soil tilth have been obtained. These changes are very pronounced on fine-textured soils (fig. 1).

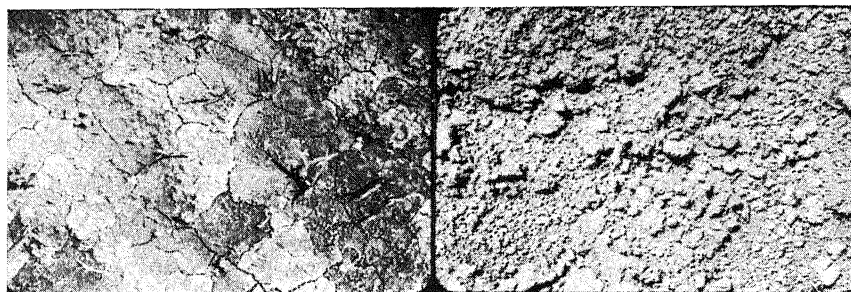


FIG. 1. EFFECT OF SOIL CONDITIONER ON PAULDING CLAY

Left, untreated; right treated with 0.15 per cent CRD-186.

All conditioners reported in this study have produced similar changes in physical properties of soils and differ, primarily, in their relative efficiency in changing soil structure.

The effect of conditioners on soil aggregation is shown by the particle-size distribution data in table 2. These data were obtained from soil samples taken in July, 1951, from field plots of Paulding clay which had been treated with CRD-186 in May of the same year. Soil samples from the top 4 inches were air-dried and analyzed by the wet-sieve procedure described by Yoder (14) and modified by Bryant *et al.* (3). This procedure involves the use of a segregated soil fraction, which, according to unpublished data at this station, results in a somewhat different aggregate-size distribution curve from that obtained with the entire soil sample. The advantage of using a segregated sample is the reduction in variability of the aggregation data. All aggregate analyses reported in this study were made on soil samples that were dry-sieved to pass through a 4.76-mm. sieve and be retained on a 2.00-mm. sieve.

Since the soil samples were not dispersed to determine degree or state of aggregation, the results in table 2 are expressed as percentage by weight of soil

TABLE 2
Effect of CRD-186 on particle-size distribution of Paulding clay

TREATMENT	PARTICLES IN VARIOUS SIZE RANGES						MEAN WEIGHT DIAMETER
	<0.25 mm.	0.25-0.50 mm.	0.50-1.0 mm.	1-2 mm.	2-5 mm.	>5.0 mm.	
Untreated	%*	%	%	%	%	%	mm.
0.05% CRD-186	55	13	12	9	10	1	0.7
0.15% CRD-186	15	5	7	10	53	10	2.6
0.15% CRD-186	6	1	1	2	71	19	3.8
LSD (0.05)	4	1	1	2	5	4	—

* By weight.

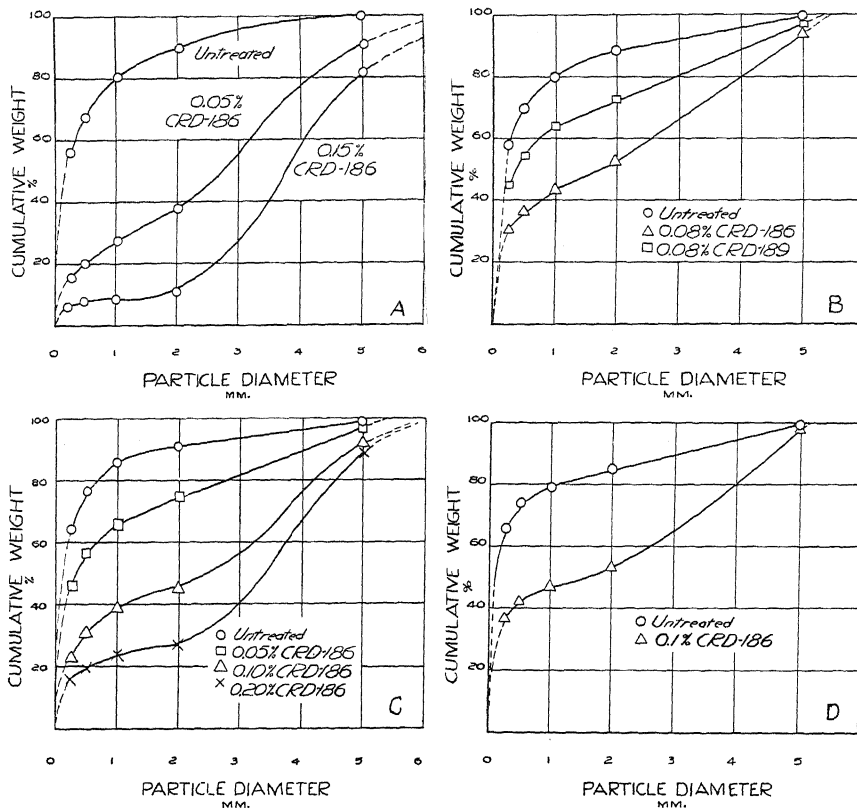


FIG. 2. CUMULATIVE PARTICLE-SIZE DISTRIBUTION OF SOILS TREATED WITH CONDITIONERS

A, Paulding clay; B, Brookston silty clay loam; C, Brookston clay loam; D, Crosby silt loam

particles (primary and secondary) within various size ranges. Mean weight-diameters were computed by the method proposed by Van Bavel (13). The data are averages of six replications in a randomized block experiment.

Table 2 shows considerable aggregation in the treated soil. The conditioner has resulted in a pronounced change in the particle-size distribution. There is a considerable shift (fig. 2-A) to larger particle sizes in soils treated with the 0.05 and 0.15 per cent rates. Perhaps a more striking effect of the conditioner is the predominance of particles produced in the 2-5-mm. and the > 5.0-mm size classes. In fact, the characteristic effect of all conditioners reported in this study is that of producing very large soil aggregates (> 2.0 mm.). It is the predominance of these large particles which gives the characteristic "crumb" appearance to the treated soil in figure 1. Particle-size distribution curves for three other soil types and two soil conditioners are shown in figures 2-B, 2-C, and 2-D.

TABLE 3
Effect of field application of CRD-186 on aggregation of three soil types

SOIL	TREATMENT	CLAY (<2 μ)	PARTICLES >2.0 MM.
		<i>per cent</i>	<i>per cent</i>
Miami silt loam.....	Untreated	25	6
	0.05% 186		24
Brookston silty clay loam.....	Untreated		8
	0.05% 186	28	33
Paulding clay.....	Untreated	45	11
	0.05% 186		63

TABLE 4
*Effect of C-I on runoff and soil erosion on Wooster silt loam**

TREATMENT	RUNOFF		EROSION
	<i>inches</i>	<i>% rainfall</i>	<i>lb./A.</i>
Untreated.....	5.70	58.80	3,430
0.5% C-I.....	0.72	7.40	31

* Data supplied by H. L. Borst, U. S. Soil Conservation Service and Ohio Agricultural Experiment Station.

It is beyond the scope of this report to discuss differences in aggregation efficiency of the various soil conditioners. It is of interest however, to note the effect of soil texture on aggregation when a conditioner is used at a constant rate. Elsewhere in this issue, Ruehrwein and Ward report that kaolinite and montmorillonite in dilute suspension are flocculated by soil conditioners. This finding, along with the data in table 3, suggests that greater aggregation might be obtained in fine-textured than in coarse-textured soils. Other factors such as organic matter content, salt content, and soil reaction probably influence the effect of conditioners on soil aggregation.

The improvement in physical properties of soil treated with soil conditioners is reflected in water runoff and soil erosion. The data in table 4 were obtained from runoff and erosion plots on Wooster silt loam with a 10 per cent slope. Treated plots received a 0.5 per cent application of C-I in the surface inch of soil after

a crop of corn had been planted, hoed, and leveled. The conditioner was incorporated in the soil surface by raking, and there were no subsequent cultivations of the plots after treatment. Total rainfall from July 3 to October 15 was only 9.68 inches. Runoff was obtained from the untreated plots after eleven rains and from the treated plots after five rains.

These data show that twice as much rainfall entered the treated soil as entered the untreated soil. Soil erosion was insignificant on the treated plots.

As one might deduce from the particle-size distribution data in table 2 and from figure 2, treatment of the soil with conditioners has changed other physical properties. In laboratory investigations of field-treated soils, significant changes in pore-size distribution and in saturated permeability have been measured. These data are given in table 5.

TABLE 5
Aggregation, aeration porosity, and saturated permeability of soils treated with conditioners

SOIL AND TREATMENT	AGGREGATION (PARTICLES > 0.25 MM.)	AERATION POROSITY	PERMEABILITY $k \times 10^5$	
			Initial	After 2 hr.
	<i>per cent</i>	<i>per cent</i>	<i>sq. cm.</i>	<i>sq. cm.</i>
Paulding clay				
Untreated.....	45	22	1.1	1.3
0.05% CRD-186.....	85	24	4.7	4.2
0.15% CRD-186.....	94	40	5.4	4.7
Brookston silty clay loam				
Untreated.....	42	23	—	—
0.08% CRD-189.....	52	29	—	—
0.08% 186.....	73	36	—	—
LSD (0.05).....	7	3	2.3	2.2

Soil cores were taken in July, 1951, from the upper 5 inches of soil which had been treated with CRD-186 and CRD-189 in May of the same year. Three cores from each plot in a randomized block experiment containing six replications were saturated, weighed, and placed on a tension plate (10) which was adjusted to give a tension of 40 cm. of water. The volume of pores drained at this tension was determined, expressed as percentage of the total soil volume, and appear under "aeration porosity" in column three.

Saturated permeability values were determined with a battery of six permeameters as described by Bloodworth and Cowley (1). Soil samples were previously saturated and subjected to a tension of 40 cm. of water for 12 hours. Permeability values were calculated for the first 10 minutes of the percolation process (initial permeability) and again for a 10-minute period after 2 hours' of percolation. The permeability, k , is calculated in absolute units of length squared from the equation:

$$\frac{Q}{t} = \frac{kdgA}{\eta} \frac{(h + l)}{(l)}$$

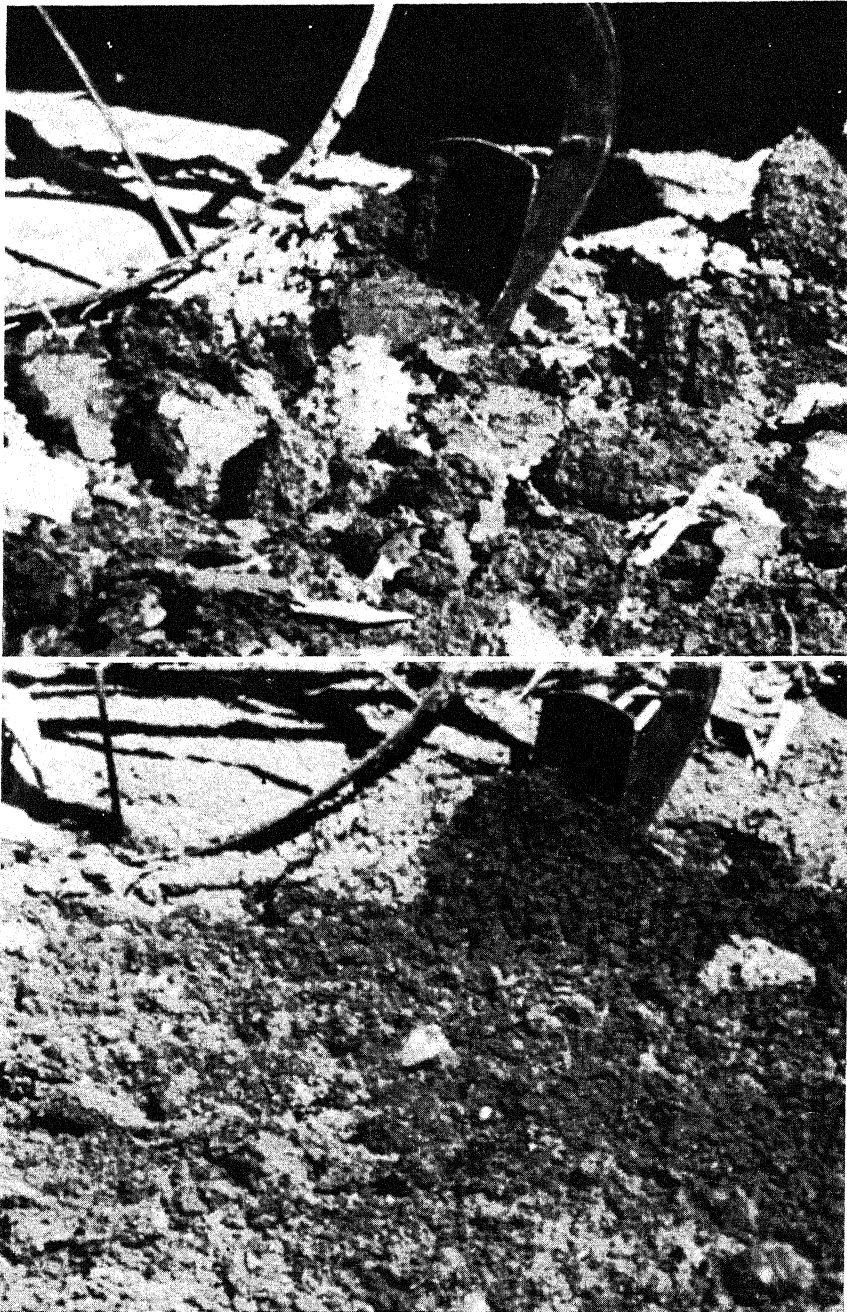


FIG 3. EFFECT OF SOIL CONDITIONER ON TILTH OF MIAMI SILT LOAM SUBSOIL
Top, untreated; bottom, treated with 0.5 per cent CRD-186 in May, 1950. Photo
taken April, 1951, prior to spring plowing.

where Q is the volume of water percolating through the soil core during time t , A is the area of the soil core of height l , and h is the height of water above the soil. The acceleration due to gravity is indicated by g ; density of water, by d ; and absolute viscosity of water, by η . All of the quantities are measured in the *cgs* system.

Table 5 shows that CRD-189 and all rates of CRD-186 increased aggregation above that of untreated soil. Although the relationships between aggregation, aeration porosity, and permeability are not strictly quantitative, increases in aggregation are reflected in greater magnitudes of the other two values. Because of the presence of large pores in the treated soil, some difficulty was encountered in obtaining an accurate weight of the saturated soil core. It is possible,

TABLE 6
Duration of aggregation produced in Miami silt loam by treatment with different soil conditioners

TREATMENT	AGGREGATION (PARTICLES > 0.25 MM.)			
	July, 1950	August, 1950	April, 1951	November, 1951*
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Untreated.....	31	31	30	28
0.05% 186.....	49	53	51	41
0.05% 189.....	43	49	44	34
0.05% C-II.....	35	32	39	30
0.50% 186.....	75	79	90	60
0.50% C-I.....	86	84	89	54
0.05% C-III.....	75	84	68	65
LSD (0.05).....	12	10	9	—

* Because of plowing, soil samples were diluted with untreated soil. Average of only two replicates.

therefore, that the "aeration porosity" figures for the treated soils are lower than the true values.

In spite of the large variation in the permeability measurement, Paulding clay treated with soil conditioner gave significantly higher values for saturated permeability than did untreated soil.

Along with the advantages of increased water infiltration, better internal drainage, and improved aeration of treated soils, the workability of soil has been improved. Treated soils are friable and loose, and are not so sticky when wet or so hard when dry as are untreated soils. The improvement in tilth of a treated soil is illustrated in figure 3, in which a garden cultivator is being pushed through adjacent plots of treated and untreated Miami silt loam subsoil.

Some residual effects of the conditioners on aggregation are given in table 6. These plots were established in a randomized block experiment containing five replications in May, 1950, to study the effect of different conditioners applied

at varying rates. The soil in the experimental area was very variable in texture, resulting in large LSD's.

Obviously, aggregation has remained significantly higher in the treated than in the untreated plots for approximately 18 months and through two cropping seasons. There is a decline in aggregation at the November, 1951, sampling date, which may be more apparent than real. In May, 1951, the area was plowed to a depth of 7-8 inches, and since the conditioner had been incorporated with the upper 4-5 inches of the soil, the samples taken for aggregate analysis in November contained untreated soil. This may be one of the reasons for the decline in aggregation at that date. Because of the empirical nature of an aggregate analysis, caution must be used in making comparisons between aggregation data at different sampling dates.

Effect on plant growth and yield

Rate and method of application (corn and soybeans). The first field experiment to test the effectiveness of soil conditioner treatment on plant growth was established on eroded Miami silt loam.⁴ The treatment variables were rates of application of CRD-186 and methods of incorporation. Field corn was used as the "indicator" crop. Essential details of the experiment are given in table 7 together with aggregation and yield results. It should be noted that in all the experiments discussed in this paper, ground preparation was essentially the same. Soils were plowed and then disked for seed bed preparation, and then the randomly selected plot areas were treated with soil conditioners. In this experiment the treatments in which the conditioner was incorporated by disk or by rototiller were made prior to planting and immediately after seedbed preparation. The topdress treatment was made just prior to the first cultivation, and CRD-186 was not incorporated with the soil.

The untreated disk-mixed and rototilled soils were less aggregated than the untreated topdress soils. Rototilling and disking are apparently destructive of natural aggregates. Conditioner treatment increased soil aggregation, the 0.1 per cent application being far more effective than the 0.02 per cent application.

Yields were increased substantially by the treatment. The variance analysis showed that the yield differences between rates of conditioner application, between methods of incorporation, and the interaction between the two were significant. The CRD-186 treatments in the disk-mixed and rototilled plots increased yields over the controls. Yield differences between the 0.02 per cent and 0.1 per cent treatments were not significant. The topdress application before cultivation was ineffective in increasing corn yields.

There was little correlation between percentage aggregation and crop yield. With the topdress treatments, this is understandable, since the changes in aggregation effected by conditioner were on the soil surface and not in the rhizosphere. In the 0.02 per cent disk-mixed and rototiller treatments, however, soil aggregation was less than in the untreated topdress treatment, and yet the yield

⁴ This experiment was established by J. B. Page, now of Texas A & M College, and F. J. Stevenson.

increase was twenty-five per cent. Furthermore, although aggregation was substantially increased by the 0.1 per cent rate over the 0.02 per cent rate in the mixed-in treatments, yield differences between the two were not significant. For explanation, reference should be made to the preceding section, which showed that the percentage of particles greater than 0.25 mm. which were water-stable in the sieve analysis (14) was not the best criterion of the structural state of the soil, since this figure is weighted in favor of the untreated soil. Conditioner treatment tends to stabilize large aggregates in the size fraction greater than 2 mm.

TABLE 7

Effect of CRD-186 on aggregation and corn yields on Miami silt loam, agronomy farm, Ohio State University, 1950

TREATMENT	AGGREGATION (PARTICLES > 0.25 MM.)	YIELD	INCREASE OVER UNTREATED	INCREASE OVER TOPDRESS
	%	(bu./A.)	%	%
<i>Topdressed</i>				
Untreated.....	36	41	—	—
0.02% 186.....	41*	40	—	—
0.10%.....	54*	42	—	—
<i>Disk-mixed</i>				
Untreated.....	29	37	—	—
0.02% 186.....	34	51	38	28
0.10% 186.....	50	54	46	28
<i>Rototilled</i>				
Untreated.....	31	34	—	—
0.02% 186.....	34	49	44	22
0.10% 186.....	50	50	47	19
LSD (0.05) (Both methods and rates of application).....		5+		

Variety: U. S. 13; 1200 plants/acre.

Planted: May 8, 1950. Harvested: Jan. 10, 1951.

Fertilizer: None.

Irrigated: No.

Plot size: 17 x 26 feet; 2 inside rows harvested.

Design: Split-plot randomized block with five replications.

* These values reflect high aggregation on soil surface. Plant roots mostly in untreated soils.

Water infiltration, aeration, and permeability are thus greatly increased by conditioner treatment, and this is sometimes not reflected in the aggregation index. This observation, however, merits further critical study and evaluation.

These soils were plowed in April, 1951, disked in May, and, without further conditioner treatment, planted to *soybeans*⁵ (Hawkeye variety). Six hundred pounds of 3-12-12 fertilizer was applied as a plowdown, and legume-bacteria-inoculated beans were planted on June 12, 1951. There were seven rows of beans

⁵ Thanks are due Lewis W. Saboe for assistance with the soybean work.

per plot, and the middle three rows were harvested on October 14, 1951. The season was extremely dry and yields were low, varying from 13 to 19 bushels per acre in different plots. Yield differences were not significant. There was some indication that the beans on the treated plots were maturing earlier than those on the untreated ones, but differences were not consistent enough to warrant a definite conclusion.

A protein analysis was made on the beans from two of the replications to determine whether the nitrogen-fixing bacteria had been more active in the structurally improved soils. The protein-nitrogen content of the beans approximated 5.9 per cent, and differences between treatments were not significant.

TABLE 8

Effect of CRD-186 on aggregation and turnip and potato yields on Brookston clay loam horticulture farm, Ohio State University, 1950 and 1951

TREATMENT	TURNIPS—1950			POTATOES—1951	
	Aggregation (particles > 0.25 mm.)	Yield/100 plants		Aggregation (particles > 0.25 mm.)	Yield†
		Roots	Leaves		
	per cent	lb.	lb.	per cent	bu./A.
Untreated.....	26	6.88	24.8	26	226
0.05% 186—1950.....	46	6.80	26.0*	41	246
0.05% 186—1951.....	—	—	—	54	262
0.05% 186—1950 and again in 1951.....	—	—	—	58	240

Variety: Purple-top White Glove turnips, 18-inch rows, thinned to 1 inch between plants; katahdin potatoes, 24-inch rows.

Planted: Aug. 21, 1950 and May 24, 1951, respectively.

Harvested: Nov. 7, 1950 and Sept. 25, 1951, respectively.

Fertilizer: 1000 pounds 5-10-10 both in 1950 and 1951.

Irrigated: Yes.

Plot size: 12.5 x 25 feet, 100 turnip plants per plot and two inside potato rows harvested.

Design: Randomized block with six replications.

* Significantly higher than control.

† Yield of U. S. No. 1 potatoes. Differences not significant.

Rate and time of application (turnips and potatoes). Brookston clay loam on the horticulture farm was also treated with CRD-186 (incorporated by rototiller) in August, 1950, and planted to turnips.⁶ Essential details of this experiment are given in table 8 together with yield results. As expected, the 0.05 per cent conditioner treatment greatly increased soil aggregation. Early turnip growth in the treated soils was substantially better than that in the controls. At the time of harvest, however, root weights were essentially the same. Better foliage development was reflected in a significantly higher weight of green leaves for 100 plants even at harvest time. As with all conditioner-treated soils, it was observed that

⁶ Appreciation is expressed to Dr. Francis E. Johnstone, Professor of Horticulture, now of the University of Georgia, for cooperation on this experiment. Dr. E. K. Alban, Associate Professor of Horticulture, has assisted with all of the work on the Horticulture Farm.

cultivation, weeding, and harvest were considerably easier than in untreated soils. The surface of the treated soils was crumbly in appearance, whereas that of the untreated soils was lumpy.

These plots were disked after harvest and allowed to stand over winter. They were disked again in May, 1951, and cross-treated with 0.05 per cent CRD-186 conditioner, converting the experiment to a factorial design with six replications as noted in table 8. Potatoes were grown as indicator crop in 1951. Potatoes were chosen because low yields in Ohio have been attributed to poor soil structure (4). Aggregation was the same in 1951 as in 1950 on the untreated soils, and very little reduction in aggregation occurred in the 1950-conditioner-treated soils during the winter period. An additional 0.05 per cent application of CRD-186 did not greatly increase soil aggregation over the single treatment.

Although the average yield of potatoes appeared to be increased by treatment, differences were not statistically significant. Yields between plots of the same treatment were extremely variable, in one instance varying from 109 to 286 bushels per acre among the six replications. Larger plots or a greater number of replications or both are in order with this crop if significant differences are to be noted between treatments.

Randomly selected potatoes from each plot were analyzed⁷ for peeling losses, specific gravity, reducing sugars, and yield and quality of potato chips. The average specific gravity was 1.0678 and the percentage yield of chips, 27.1, all of good quality. There were no significant differences between treatments in these properties.

Rate of application (potatoes and carrots). The rate of application of soil conditioner was increased above 0.05 per cent to determine the effect on crop yields. A plot of Brookston clay loam on the horticulture farm and adjacent to the area described in table 8, was treated with CRD-186 at rates of 0.1 per cent and 0.2 per cent. The conditioner was incorporated by rototiller. Potatoes, for comparison with results in the preceding experiment, and carrots were used as test crops. The carrots were weeded with "Stoddard's Solvent," so that after planting no disturbance of the soils occurred.

Other details of the experiment together with yield results are given in table 9. The untreated soils of this area were more highly aggregated than those of table 8 and the higher rates of conditioner treatment effected very high states of soil aggregation. Potato yields were lower, however, than those in the adjacent area. Again, yields between plots in the same replication were so variable that statistically significant differences were not obtained.

Potatoes from these plots also were analyzed for differences in specific gravity and in yield and quality of potato chips. Differences again proved to be nonsignificant.

With carrots, however, statistically significant yield increases occurred as a result of treatment. Gross weights, which approximated 20 tons of carrots per acre, did not differ significantly between treatments. Grading into marketable

⁷ By W. A. Gould.

size, however, showed that conditioner treatment did effect a marked increase in yield.

Both the carrots and the potatoes in the treated soil were more easily dug and came out of the ground clean. The untreated soils were hard and cloddy and adhered to the carrots and potatoes.

Type of conditioner and method of application (sugar beets). A heavy-textured Brookston silty clay loam on the agronomy farm was used in an experiment to determine the relative effect of conditioners CRD-189 and CRD-186 on soil aggregation and crop yields. A comparison between disking and rototilling as methods of incorporation was also one of the objectives. The desirability of remixing after 24 hours to obtain maximum aggregation was also tested. Sugar

TABLE 9

Effect of CRD-186 on aggregation and potato and carrot yields on Brookston clay loam, horticulture farm, Ohio State University, 1951

TREATMENT	AGGREGATION (PARTICLE > 0.25 MM.)	POTATOES U.S. NO. 1	MARKETABLE CARROTS	
			Yield	Increase over untreated
	<i>per cent</i>	<i>bu./A.</i>	<i>tons/A.</i>	<i>per cent</i>
Untreated.....	36	212	15.4	—
0.10% 186.....	77	223	17.1	11
0.20% 186.....	84	218	18.7	21
LSD (0.05).....	4	Not significant	1.4	

Variety: Katahdin potatoes, 24-inch rows; red-cored Chantenay carrots, 12-inch rows.

Planted: May 24, 1951. Harvested: Sept. 25, 1951.

Fertilizer: 1000 pounds 5-10-10.

Irrigated: Yes.

Plot size: 12.5 x 25 feet, two inside potato rows and four inside carrot rows harvested.

Design: Randomized block with four replications.

beets were used as the test crop. Other essential details of the experiment are given in table 10 together with aggregation and yield results.

In contrast with the Brookston soil of the horticulture farm, soil aggregation in the untreated soils was high, even though this was considered to be a "problem" soil. Incorporation of 0.08 per cent CRD-189 or CRD-186 significantly increased soil aggregation, CRD-186 being considerably more effective at the same concentration than CRD-189. Differences in the percentage of water-stable aggregates resulting from disking as contrasted with rototilling were not significant, nor were significant differences in aggregation effected by remixing in 24 hours.

No statistically significant sugar beet yield increases occurred as a result of treatment. The beets in the rototilled plots were better than those in the disked plots. This does not correlate with structural differences and no explanation is offered for this observation. Sugar beet yields were high for this area. As with the other root crops, the beets were more easily dug and came out of the ground clean.

Another observation was that the CRD-186-treated plots were definitely less weedy than the others. This was attributed to the tendency of these soils to dry out more quickly at the surface after precipitation, which probably hindered germination. The CRD-189-treated soils did not show this effect.

Rate and method of application for oats and alfalfa. In another experiment, Crosby silt loam on the agronomy farm was treated with CRD-186 in three ways: (a) mixed with the top 4 to 6 inches with a "culti-mulcher," equivalent to disk-mixing; (b) placed on the surface and incorporated lightly with a rake; and (c)

TABLE 10

Effect of CRD-186 and CRD-189 on aggregation and sugar beet yields on Brookston silty clay loam, agronomy farm, Ohio State University, 1951

TREATMENT		AGGREGATION (PARTICLES > 0.25 MM.)	YIELD
		per cent	tons/A.
Untreated			
Disk-mixed		42	20.8
Rototilled		42	23.6
0.08% 189			
Disk-mixed		58	21.4
Rototilled		52	24.2
0.08% 186			
Disk-mixed		68	20.4
Rototilled		73	23.6
LSD (0.05)	Kind conditioner	7	Not significant
	Method of application	Not significant	1

Variety: Unknown, 24-inch rows, thinned to 6 inches between plants, 1750 plants per acre.

Planted: May 17, 1951. Harvested: Oct. 25, 1951.

Fertilizer: 1000 pounds 4-16-8; 50 pounds N sidedressed July 17, 1951.

Irrigated: Yes.

Plot size: 8 x 22 feet, two inside rows harvested.

Design: Double split-plot randomized block with six replications.

Note: At the time of application, half of each plot was disked or rototilled again in 24 hours; there was no significant improvement in soil aggregation or yield. The above figures are thus the average of 12 replications.

drilled in with the fertilizer. For the sake of uniformity, all plots were culti-mulched before being given other treatments. Rates of application in all treatments were estimated to be the same for the soil brought into contact with the conditioner. Rates per acre, however, varied markedly, and these are the ones recorded in table 11. This experiment was designed to test the effect of conditioner treatment on the establishment and growth of alfalfa⁸ and also of the oats nurse crop. Alfalfa is one of the difficultly established small-seeded legumes. As improvements in stand have occurred with band-seeding (9) over the fertilizer, this

⁸ Appreciation is expressed to R. L. Jeffers for assistance on this experiment.

procedure was followed in these tests. Other essential details of the experiment are given in table 11 together with aggregation and yield results.

Soil aggregation was markedly increased by 0.1 per cent CRD-186 disk-mixed with the soil, and Clinton oats yielded 40 per cent higher in these soils. Plants averaged almost a foot taller in the plow-furrow-treated soils. This was one of the most spectacular responses to conditioner treatment noted among the experiments herein recorded.

Aggregation, as expected, was not much affected by the surface application and drilled conditioner treatments. With the rhizosphere largely untreated, oats in the surface-treated soils did not yield significantly higher than the controls. A marked reduction in yield occurred when the seed was drilled with CRD-186.

TABLE 11

Effect of CRD-186 on aggregation and oat yields on Crosby silt loam, agronomy farm, Ohio State University, 1951

TREATMENT	AGGREGATION (PARTICLES > 0.25 MM.)	YIELD	DEVIATION FROM UNTREATED
	<i>per cent</i>	<i>bu./A.</i>	<i>per cent</i>
Untreated.....	34	30	—
0.10% 186 disk-mixed.....	63	42	+40
0.03% 186 on surface.....	40	32	—
0.01% 186 drilled with seed and fertilizer.....	35	23	-23
LSD (0.05)	3	6.2	

Variety: Clinton oats and Kansas Common alfalfa.

Planted: April 28, 1951. Harvested: July 26, 1951.

Fertilizer: 450 pounds 0-15-15.

Irrigated: No.

Plot size: 8 × 90 feet, 7 × 80 feet harvested.

Design: Randomized block with six replications.

Note: *Alfalfa* was band-seeded over fertilizer. There were no significant stand differences.

This reduction was largely the result of decrease in stand. In large concentrations, the conditioner becomes gelatinous. It also has high alkalinity. It is postulated that under these conditions germination is reduced. This observation is worthy of further critical study and evaluation.

Alfalfa yields will be taken on these plots in 1952. Because of a tendency for the CRD-186-treated soils to dry out on the surface more quickly following precipitation, it was feared that the stand might be reduced. When the number of plants in several randomly placed square-yard areas per plot were counted in September, 1951, however, no significant differences between treatments were obtained.

Rate of application on Paulding clay (sweet corn and beets). One of the most critical areas in Ohio so far as soil structure is concerned is the heavy lacustrine clay area of the Northwest. These soils with proper drainage have been among

the most productive in the corn belt. They are becoming heavier, however, and drainage is a critical problem. It is in this area that Page and Willard (12) obtained remarkable yield increases from rotation versus continuous row-cropping. This was attributed to improvement in soil structure. It was considered desirable, therefore, to utilize the soil-conditioning chemicals in this area for comparison with the results obtained by Page and Willard.

A plot of Paulding clay near Paulding, Ohio, was therefore treated with CRD-186 at rates of 0.05 per cent and 0.15 per cent incorporated by disking. Because of the heavy cloddy nature of the soil, it was disked several times for thorough mixing. The field used had been in tomatoes in 1950, had been fall plowed, and was disked for sugar beets in May, 1951. Treatments were made May 18, 1951, and sugar beets were planted immediately. Root rot killed most of the beets.

TABLE 12

Effect of CRD-186 on aggregation and sweet corn and beet yields on Paulding clay, Paulding County experiment fields, Ohio Agricultural Experiment Station, 1951

TREATMENT	AGGREGATION (PARTICLES > 0.25 MM.)	SWEET CORN		RED BEETS	
		Height	Increase over untreated	Weight/30-foot row	Increase over untreated
	<i>per cent</i>	<i>in.</i>	<i>per cent</i>	<i>lb.</i>	<i>per cent</i>
Untreated.....	45	12.1	—	6.7	—
0.05% 186.....	85	21.3	76	7.7	15
0.15% 186.....	94	24.4	102	8.7	30

Variety: Mar-Cross sweet corn, 40-inch rows, 8 inches apart in rows. Detroit Dark Red beets, 12-inch rows, unthinned.

Planted: Aug. 2, 1951 and Aug. 9, 1951, respectively.

Harvested: Sept. 18, 1951 and Oct. 12, 1951, respectively.

Fertilizer: 300 pounds 3-12-12 plowdown and 300 pounds 3-12-12 in the row.

Irrigated: No.

Plot size: 16 × 25 feet, 29–45 plants per plot of sweet corn measured and 30 feet of row of beets.

Design: Randomized block with six replications.

Early sweet corn and red beets were planted in August in a "salvage" operation. These were grown until killed by frost, at which time height and weight measurements were taken. Yield results for these crops together with other essential details of the experiment are given in table 12.

As noted in an earlier section, conditioner treatment effected marked increases in soil aggregation and related features. Corresponding with this improvement in structure were marked plant responses. Sweet corn almost doubled in height as a result of treatment, and weight of unthinned red beets increased substantially. Many of the beets in the treated plots, but none in the untreated, were ready for table use (1 + inches in diameter) at time of harvest.

SUMMARY

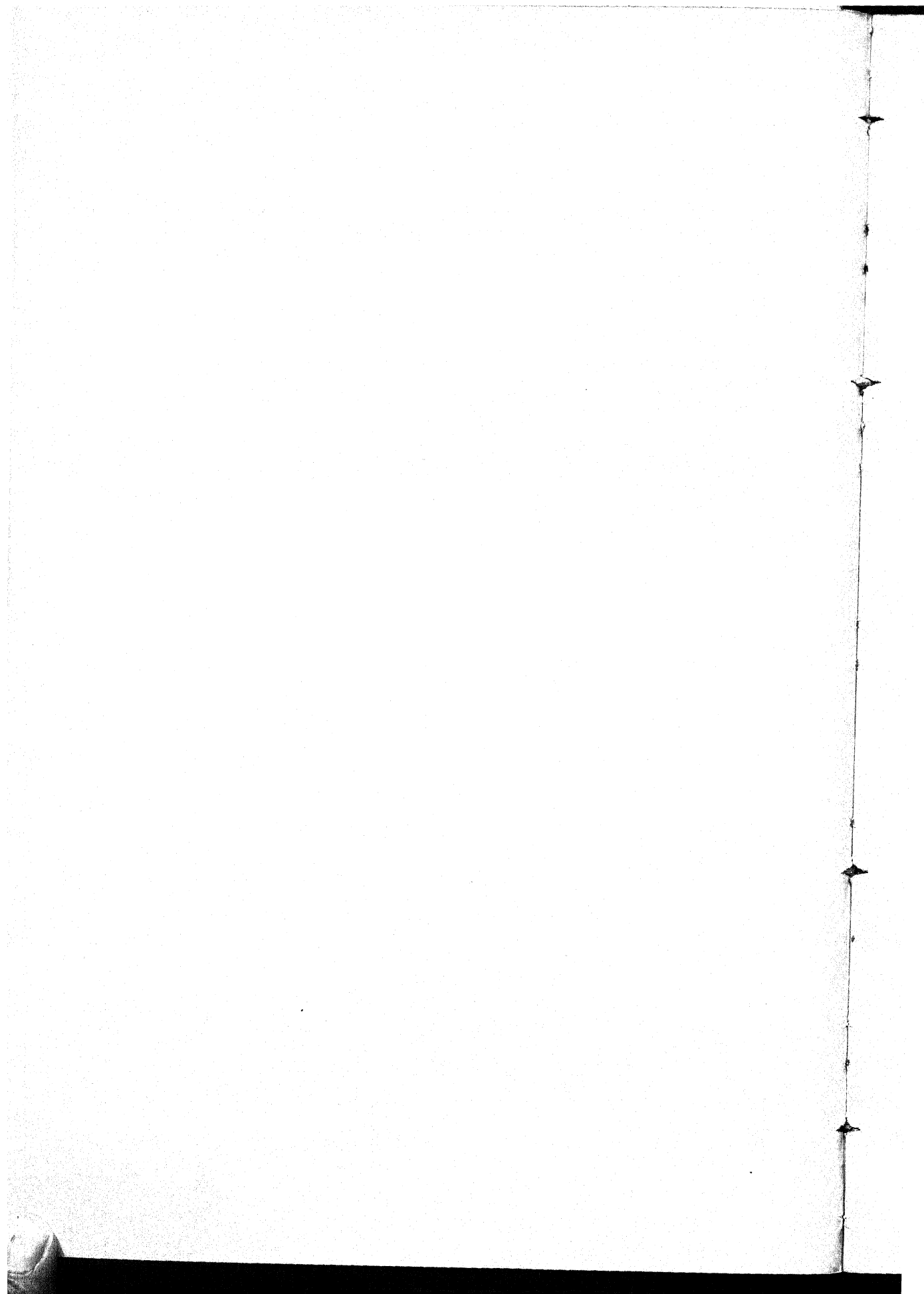
The effect of Krilium soil conditioners on the physical properties of heavy-textured Miami, Crosby, Brookston, and Paulding soils was studied. Applica-

tions at rates varying from 0.02 to 0.20 per cent and in powder form to these soils in the field, with subsequent mixing by disking and rototilling, without exception, increased soil aggregation and such related characters as porosity and permeability. Large crumbs (aggregates larger than 2 mm.) were most commonly produced, total aggregation often exceeding 80 per cent. Moreover, the aggregates proved to be water-stable and the conditioning chemicals highly resistant to decomposition. Structural improvement persisted through the second growing season.

The effect of Krilium treatment on the growth of many crops was tested in statistically controlled field experiments. Not all crops responded to treatment, although in many instances yields increased appreciably. Corn, oats, and carrots were most responsive to conditioner treatment. No toxicities were noted.

REFERENCES

- (1) BLOODWORTH, M. E., AND COWLEY, W. R. 1951 Use of undisturbed soil cores for permeability and infiltration determinations. *Jour. Amer. Soc. Agron.* 43: 4-8.
- (2) BOUYOUKOS, J. W. 1930 Comparison of the hydrometer method and the pipette method for making mechanical analysis of soils, with new directions. *Jour. Amer. Soc. Agron.* 22: 747-751.
- (3) BRYANT, J. C., BENDIXEN, T. W., AND SLATER, C. W. 1948 Measurement of water stability of soils. *Soil Sci.* 65: 341-345.
- (4) BUSHNELL, J. 1949 Potato soils and some problems in handling them. *Ohio Veg. and Potato Grower's Assoc. Proc.* 34: 70-75.
- (5) COCHRAN, W. G., AND COX, G. M. 1950 Experimental Designs. John Wiley & Sons, Inc., New York.
- (6) CONREY, G. W., PASCHALL, A. H., AND BURRAGE, E. M. 1948 A key to the soils of Ohio. Ohio Agr. Exp. Sta. Spec. Cir. 78.
- (7) DICKMAN, S. R., AND BRAY, R. H. 1941 Replacement of absorbed phosphate from kaolinite by fluoride. *Soil Sci.* 52: 263-273.
- (8) GORTNER, R. A. 1916 Organic matter of the soil: I. *Soil Sci.* 1: 395-442.
- (9) HAYNES, J. A., AND THATCHER, L. E. 1950 Band seeding method for meadow crops. *Ohio Farm Home Res.* 35: 3-5.
- (10) LEAMER, R. W., AND SHAW, B. 1941 Simple apparatus for measuring noncapillary porosity on an extensive scale. *Jour. Amer. Soc. Agron.* 33: 1003-1008.
- (11) MCCREADY, R. M., AND HASSID, W. Z. 1942 Semimicro determination of carbon. *Indus. and Eng. in Chem., Analyt. Ed.* 14: 525.
- (12) PAGE, J. B., AND WILLARD, C. J. 1947 Cropping systems and soil properties. *Soil Sci. Soc. Amer. Proc.* (1946) 11: 81-88.
- (13) VAN BAVEL, C. H. M. 1950 Mean weight-diameter of a soil aggregates as a statistical index of aggregation. *Soil Sci. Soc. Amer. Proc.* (1949) 14: 20-23.
- (14) YODER, R. E. 1936 Direct method of aggregate analysis of soils and a study of the physical nature of erosion losses. *Jour. Amer. Soc. Agron.* 28: 337-350.



EFFECT OF SYNTHETIC SOIL CONDITIONERS ON EROSION CONTROL

LLOYD E. WEEKS AND WILLIAM G. COLTER¹

Central Research Laboratories, Monsanto Chemical Company

Soil losses resulting from the action of rainfall have presented a tremendous problem to man since the beginning of recorded time. The impact of a raindrop on unprotected soil breaks down structure, and surface flow transports the detached soil. This action results in either sheet or gully erosion. A well-known measure to effect good control of the erosive action of water is the establishment of a vegetative cover where soil will support it. Grasses suitable for the location under consideration are commonly established to serve this purpose, as they cushion the fall of raindrops, minimizing the slaking or detachment of soil particles. With surface soil stabilized in this manner, infiltration is enhanced and runoff, which carries away valuable soil, is reduced.

Since grassed areas are usually established by seeding, it is necessary to control erosion temporarily until the grass is adequately developed. Vegetative mulches usually consisting of straw or hay are generally applied over newly seeded sloping surfaces. Disadvantages of mulches are flammability, bulk, unsightliness, high application costs, and in many instances unavailability.

Experiments with synthetic soil conditioners for improving soil structure, have led to the study of these materials for erosion control applications. These compounds consist of the sodium salt of hydrolyzed polyacrylonitrile (CRD-189-A) and a calcium carboxylate polymer (CRD-186-1). Application of these chemicals to soil surfaces results in a permeable film which is resistant to the impact of raindrops, yet does not interfere with, in fact, appears to improve, the development of vegetation. A series of practical tests demonstrated the conditioners to be so outstanding in controlling erosion that it was decided to conduct both field and laboratory evaluations.

EXPERIMENTAL

Some properties of the soil conditioners are presented in table 1.

Their effect upon soils can be demonstrated by the manner in which they modify soil consistency. Figures 1, 2, and 3 are plots of liquid and plastic limits versus conditioner concentrations in three different soils.

These data show that very small amounts of the conditioners greatly modify soil consistency characteristics by almost doubling liquid and plastic limits in some cases. The maximum points in the plastic limit curves indicate that there may be a limit to the amount of conditioner the soil will adsorb and any excess lowers the consistency.

¹ The preparation of the high-speed movies and other photography by Sarah J. Aulbaugh and the assistance of T. W. Saloman on the slope project are gratefully acknowledged. Suggestions by L. V. Sherwood, D. T. Mowry, R. G. Fordyce, and C. A. VanDoren (Soil Conservationist, U.S. Department of Agriculture) were especially helpful.

A simple demonstration of the effectiveness of the conditioners in stabilizing surface soil was made by allowing water drops to fall upon treated and untreated soils and recording the results with high-speed movie photography. After being graded through a 10-mesh sieve, Dayton alluvial soil was placed in trays. One tray was treated by spreading CRD-189-A at 1 pound per 100 square feet on the surface and wetting down to dissolve the polymer. The other tray served as a control. The impact on the soil surfaces by water droplets falling from a height of 12 feet was photographed at a speed of about 3,500 frames per second.

Figure 4 presents the before and after effects of the water drops. The stability of treated soil is demonstrated by absence of soil splashed upon the white background.

TABLE 1
Physical properties of soil conditioners

	CRD-186-1	CRD-189-A
Rate of solution in water.....	Rapid	Rapid
Stability to acids.....	Gels slowly	Precipitates
Excess Ca ⁺⁺ , Al ⁺⁺⁺	Precipitates	Precipitates
Effect of formaldehyde.....	None	Gels
Brookfield viscosity of 1.0% aqueous solution in poises.....	1.2	1.7
pH Values		
At 0.1%.....	5.4	10.4
At 1.0%.....	4.9	11.4
Bulk Density, in lb./cu. ft.....	42.8	42.2

	PARTICLES					Passing Through Sieve No. 200
	Retained on Sieve Nos.					
	20	40	80	140	200	
	%	%	%	%	%	
CRD-186-1	0.1	0.3	2.4	14.7	24.7	57.8
CRD-189-A	0.2	3.0	31.3	19.2	14.4	32.1

This simple experiment, along with information obtained from some practical tests, led to field experiments on slopes where the performance of the conditioners could be evaluated under semicontrolled conditions. Two ridges were constructed of Dayton alluvial soil. Each ridge was approximately 100 feet long and had a slant length for each side of 8 feet with a 2-foot horizontal section on the crest. One ridge had a gradient of 34° (1 on 1½) and the other 22° (1 on 2½). The soil, being slightly moist during construction, was well compacted by the equipment used. Field density determinations made on the top 3-inch layer of soil gave density values of about 85 pounds (dry weight) per cubic foot.

Plots 4 feet wide by 8 feet long (base to crest) were laid out. Galvanized sheet metal strips 6 inches wide extending 4 inches above the surface were used as side borders. Near the base of the slope was inserted a strip of galvanized sheet metal

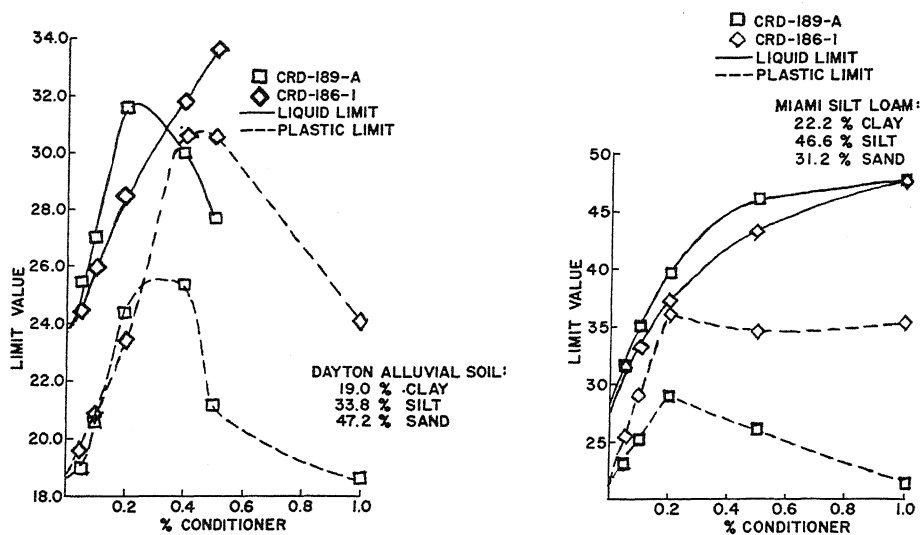


FIG. 1. (left) EFFECT OF SOIL CONDITIONERS ON LIQUID AND PLASTIC LIMITS OF DAYTON ALLUVIAL SOIL

FIG. 2. (right) EFFECT OF SOIL CONDITIONERS ON LIQUID AND PLASTIC LIMITS OF MIAMI SILT LOAM

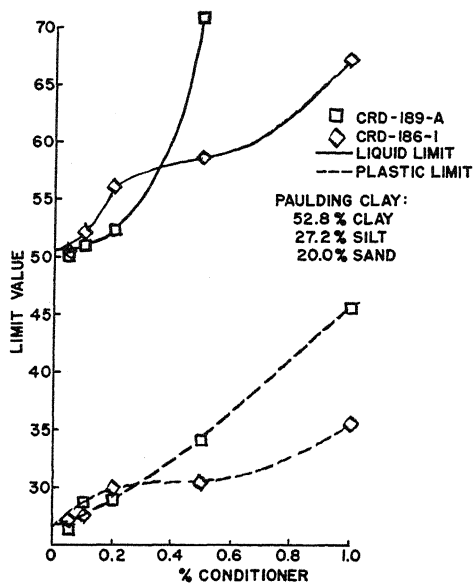


FIG. 3. EFFECT OF SOIL CONDITIONERS ON LIQUID AND PLASTIC LIMITS OF PAULDING CLAY

to serve as a drainboard. This drain was 10 inches wide and was half buried in the slope. At the lower corner of each plot, the side borders were connected to the drainboard by a concrete junction.

Where data on soil movement only was desired, soil collectors consisting of cloth filters mounted on a wooden framework were installed below the drain-board. This installation was employed on the 34° slopes. The eroded soil was collected and the dry weight periodically determined.

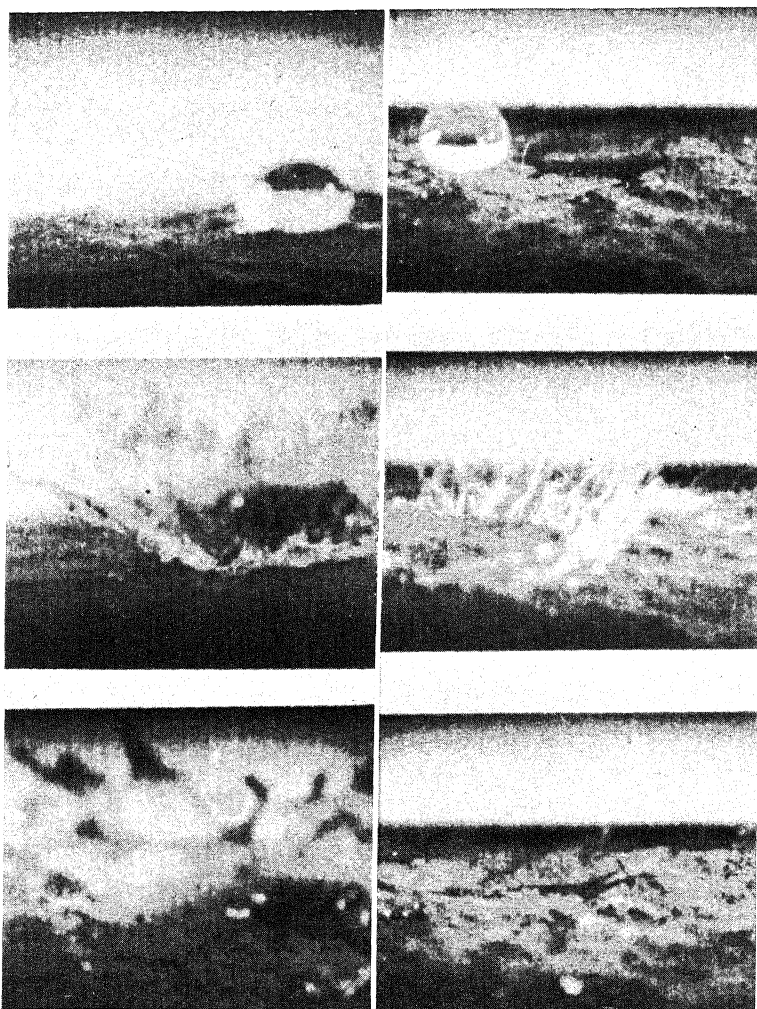


FIG. 4. EXCERPTS OF SPLASH TESTS ON DAYTON ALLUVIAL SOIL FROM HIGH-SPEED MOVIE PHOTOGRAPHY

Left, untreated soil: note splash on white background card in last sequence and also turbidity of water. Right, treated soil: water is clear and no soil splashed.

Runoff and soil movement data on the 22° slope were obtained from tanks placed below the drainboard. Runoff measurements were made periodically during each application of water. For information on soil movement, cloth filters inside the tanks facilitated the separation of soil from water.

Artificial rainfall was applied to the slopes by means of Skinner irrigation equipment (Skinner Irrigation Company, Troy, Ohio). A tapering pipe mounted $4\frac{1}{2}$ feet above and at approximately right angles to the midpoint of the slopes, carried the water. Artificial rainfall was generated by nozzles (Type SS 70°) spaced at 2-foot intervals which provided a uniform fan-shaped spray pattern. The irrigation line or pipe was rotated by an oscillator which moved the spray up and down the slope at a rate of one complete cycle per minute. This system produced a very high intensity rainfall which slowly swept up and down the

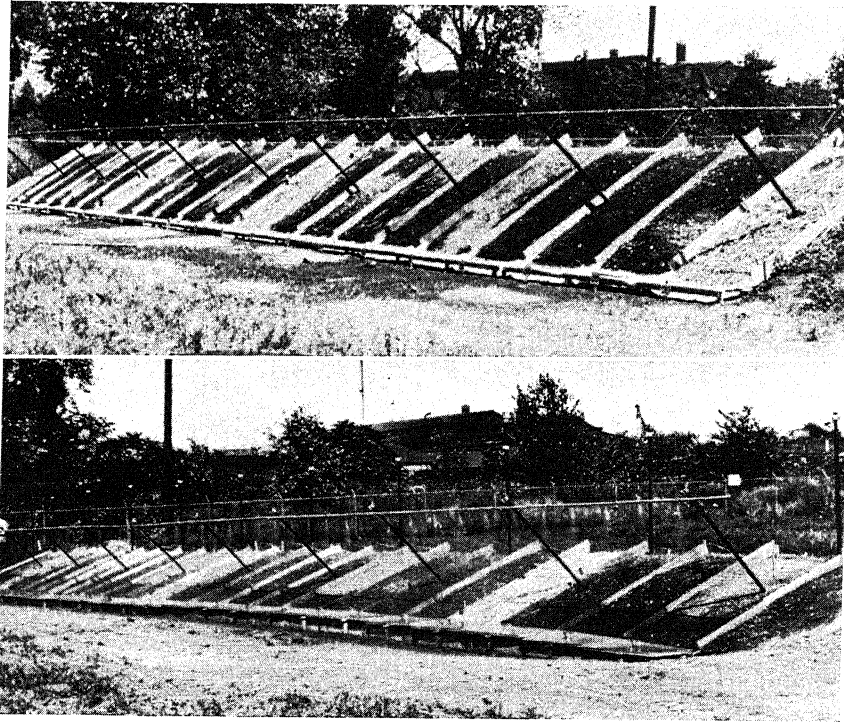


FIG. 5. SLOPES USED FOR EROSION TESTS

Above, 34° slope; below, 22° slope

plots. The droplet size of the spray, however, was much smaller than that for the average natural rain. An estimate of droplet size would be 1 to 3 mm. diameter, versus natural rainfall at about 5 mm. diameter. The intensity applied was 2.7 to 3.0 inches per hour with a line pressure of 53 to 60 pounds per square inch.

Figure 5 shows the slopes after the plots were installed.

Observations on natural rainfall were recorded by a rain gauge. Here the average intensity for the entire period of rainfall was used. Total natural rainfall was only 4.24 inches for the entire test period from July 11 to October 16. The maximum average intensity was 0.4 inch per hour, and the maximum rainfall for any one period was 0.58 inch.

Prior to treatment of the plots, the soil was loosened and broken by raking to a depth of 1 inch. The conditioners were applied by two methods: first, the conditioner was distributed uniformly over the surface, raked in to about $\frac{3}{4}$ inch, and wet down with a fine water spray to dissolve the conditioner; second, conditioner was distributed uniformly over the surface and then wet down to form a surface film. Seed was sown after the raking-in treatment but prior to wetting down, and in advance of the surface method of conditioner application. The seed, consisting of a mix containing 40 per cent Kentucky bluegrass, 25 per cent red-

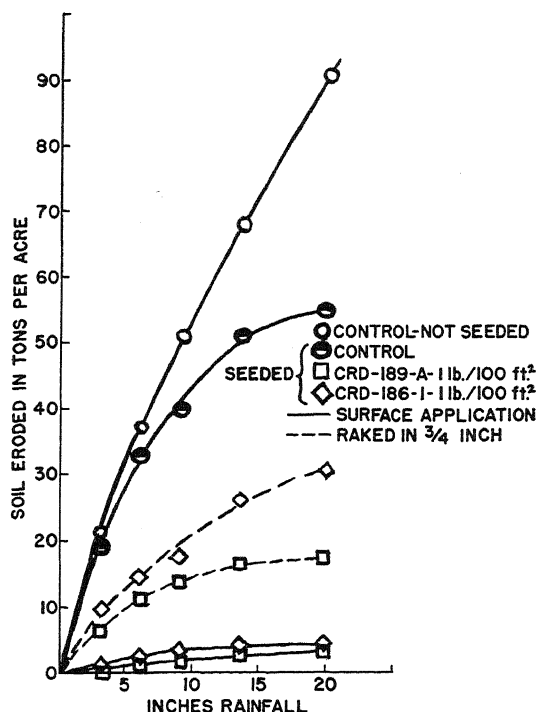


FIG. 6. SOIL MOVEMENT FOR TWO METHODS OF CONDITIONER APPLICATION ON A 34° SLOPE (5-WEEK PERIOD)

top, 30 per cent domestic ryegrass, and 5 per cent white clover, was broadcast by hand over the plots and raked in to a depth of about $\frac{1}{4}$ inch.

Where plots were mulched, straw was applied and tied down in a criss-cross manner with cord to stakes spaced at 4-foot intervals.

RESULTS

Soil movement

A series of plots was established on July 11, to determine which method of conditioner application was most effective in controlling erosion. Artificial rainfall was applied for $\frac{1}{2}$ -hour periods starting on the day after the plots were installed and continuing at the rate of two to three waterings a week for 5 weeks.

Data obtained for these plots are presented in figure 6. The plots, at the end of 3 weeks and after 15 inches of rain was applied, are shown in figure 7.

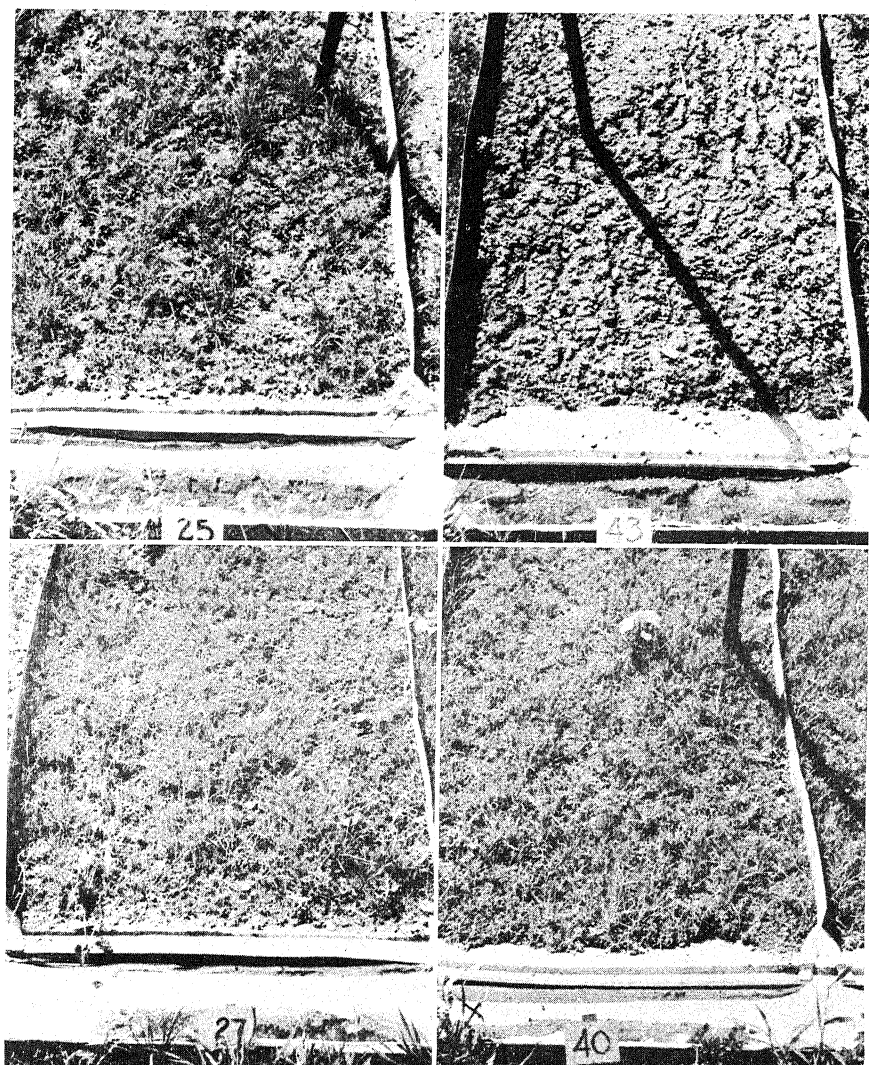


FIG 7. EFFECT OF TWO METHODS OF CONDITIONER APPLICATION ON PLOTS
AT THE END OF 3 WEEKS AND AFTER 15 INCHES OF RAIN

Plot 25, seeded control; plot 43, unseeded control; plot 27, 1 pound CRD-189-A per 100 square feet raked in; plot 40, 1 pound CRD-189-A per 100 square feet applied to surface.

The first test-series prompted the installation of a second series on August 16, in which the plots were replicated four times in a randomized fashion. The conditioner was applied entirely by the surface method and the same watering procedure was used as in the previous series. Results from this test are presented in

figure 8, in which averages of soil losses are plotted against rainfall. Figure 9 shows the series near the beginning of the test, and figure 10, after 5 weeks.

On the 22° slope, plots were established to obtain data on both soil movement and runoff. Plots were prepared on September 4. Here water was applied for 1-hour periods twice a week for the first 3 weeks and once a week for the remaining 3 weeks. Three replications of randomized blocks were made of each treatment.

Figure 11 presents data on soil eroded in this series. All of the data obtained demonstrated that CRD-189-A, in particular, was effective in stabilizing soil to rain erosion.

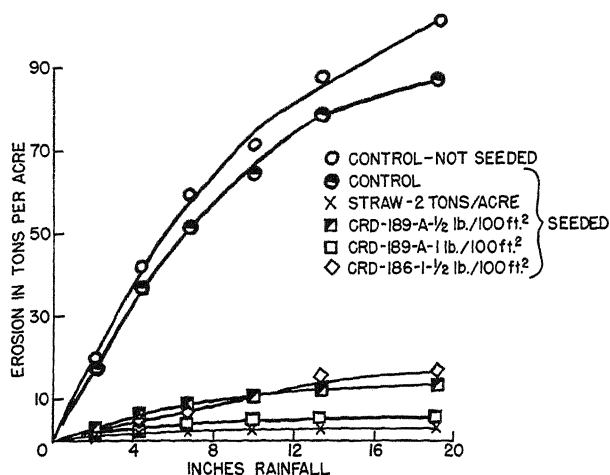


FIG. 8. EROSION CONTROL ON A 34° SLOPE WITH CRD RESINS (5-WEEK PERIOD)

Runoff

Runoff data for plots treated with mulch, CRD-189-A, and controls are presented in figure 12. The performance of CRD-189-A in reducing runoff was similar to that for mulch.

Statistical evaluation of data

The limits for the variation of data in a replicated group were taken as $\bar{x} \pm 2 \sqrt{\frac{\sigma}{n-1}}$, where \bar{x} is the mean and σ is the standard deviation. This treatment provides a 95 per cent confidence level.

DISCUSSION

Application

Of the two methods of applying conditioner, the surface treatment was found to be at least twice as effective as the raked-in treatment.

For very small areas, hand-broadcasting of the conditioners has been found suitable. For larger plots where the terrain is not steep, the conditioners can be

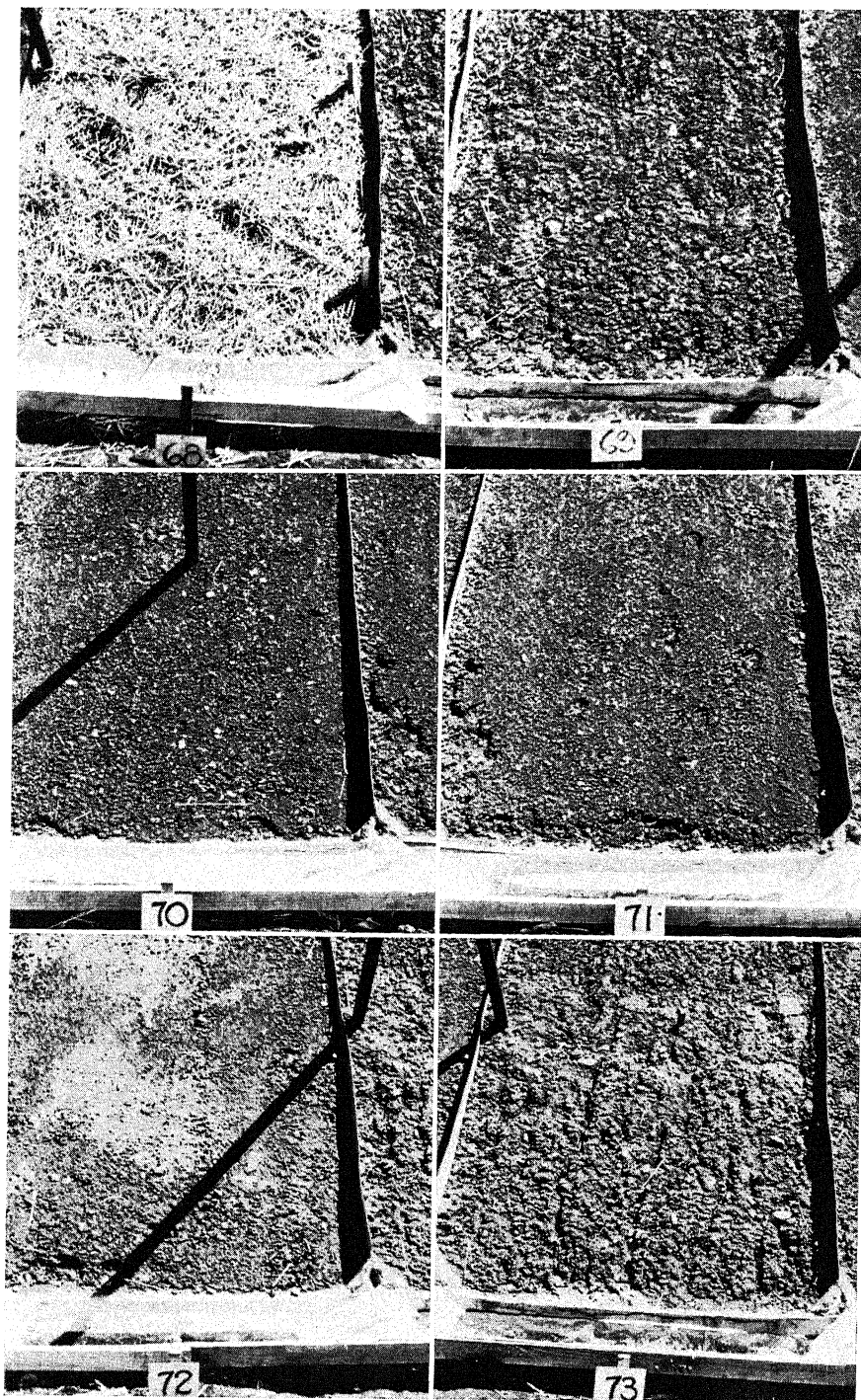


FIG. 9. EROSION CONTROL ON REPLICATED PLOTS 1 WEEK AFTER TREATMENT
AND AFTER 4 INCHES OF RAIN

Plot 68, 2 tons straw per acre; plot 69, unseeded control; plot 70, 1 pound CRD-189-A per 100 square feet; plot 71, $\frac{1}{2}$ pound CRD-189-A per 100 square feet; plot 72, $\frac{1}{2}$ pound CRD-186-1 per 100 square feet; plot 73, seeded control.

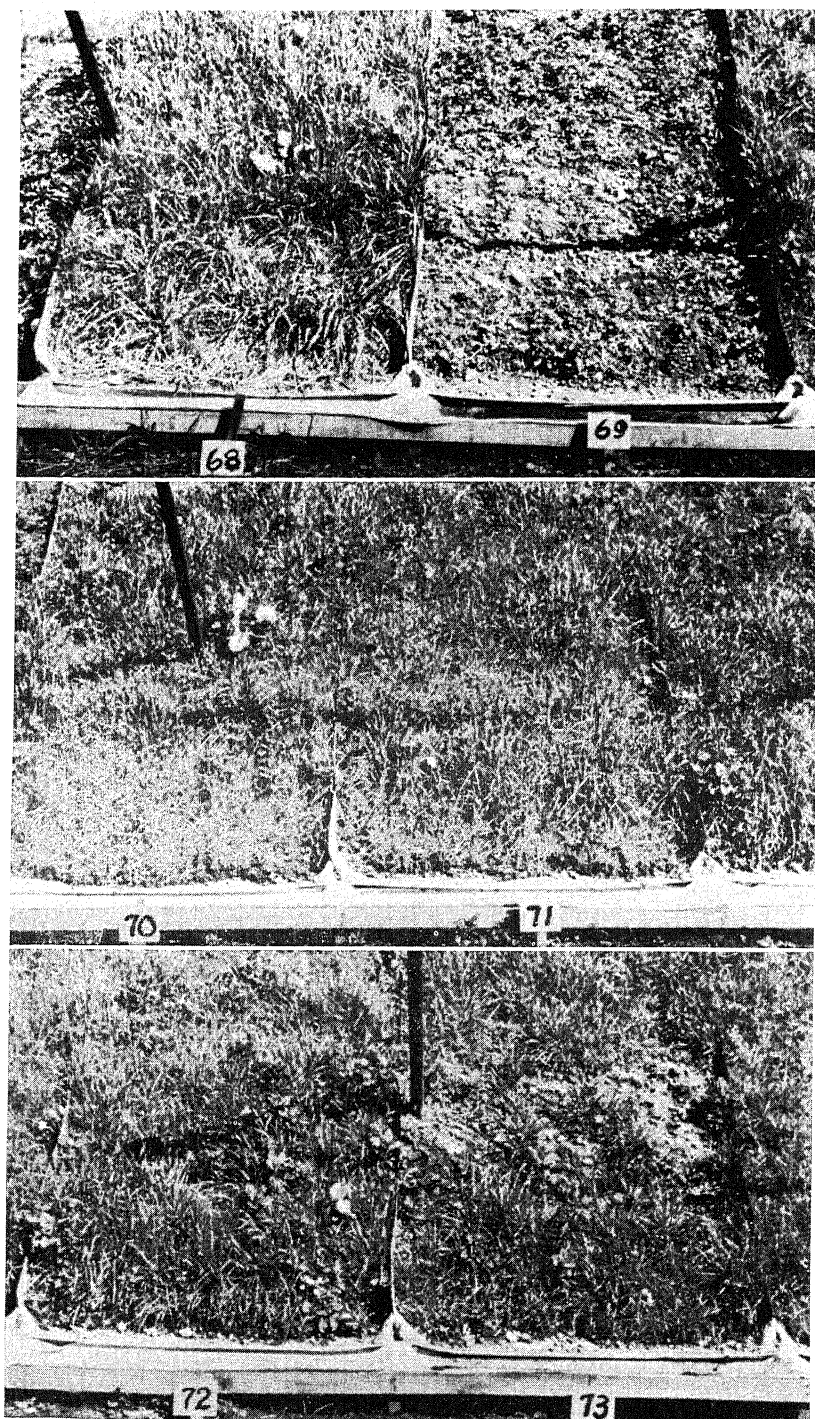


FIG. 10. EROSION CONTROL ON REPLICATED PLOTS 5 WEEKS AFTER TREATMENT
AND AFTER 19 INCHES OF RAIN
Plots are those shown in figure 9.

satisfactorily applied with any fertilizer spreader that will provide uniform distribution. For large-scale operations, equipment is currently being developed to apply the conditioners in the form of a liquid spray.

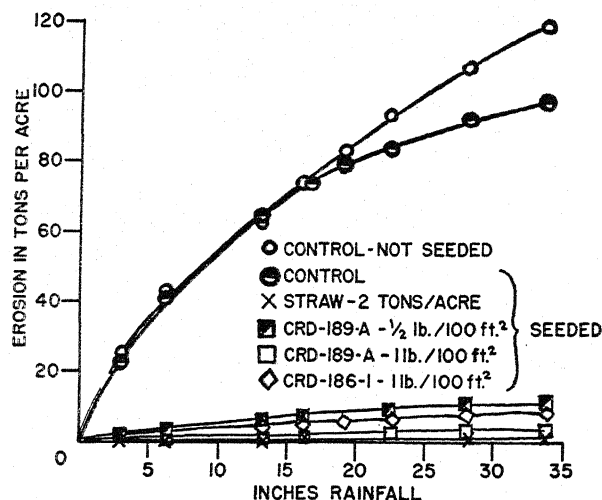


FIG. 11. EROSION CONTROL ON A 22° SLOPE WITH CRD RESINS (6-WEEK PERIOD)

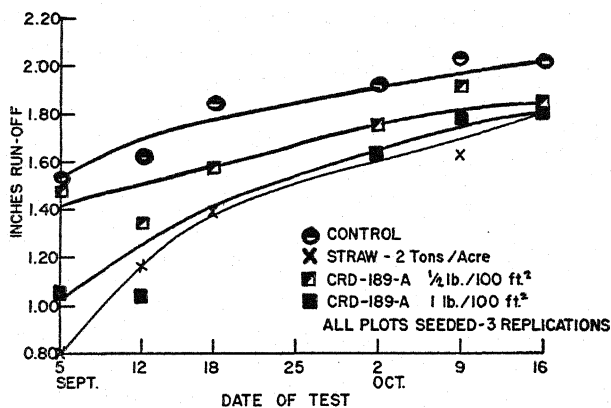


FIG. 12. RUNOFF ON A 22° SLOPE OVER A 6-WEEK PERIOD

2.8 inches of rain applied during each test

Performance

Both CRD-186-1 and CRD-189-A gave good control of soil movement; CRD-189-A, however, was the better. Grass germination on plots treated with CRD-189-A was superior to that on plots treated with CRD-186-1. This is believed to be due to higher surface moisture content of CRD-189-A plots, since the conditioner is hygroscopic.

The present data show that CRD-189-A is about as effective in reducing erosion and runoff as is mulch. For controlling soil losses, CRD-189-A in most cases ranged from equal to half as effective as mulch.

In a special test where a coarse water spray was applied to plots treated with CRD-189-A and with straw mulch and to a control plot, the effectiveness of the conditioner was comparable to that of the mulch. The water was applied at a rate of about 7 inches an hour for 15-minute intervals. This system was used to determine the effectiveness of CRD-189-A under very drastic conditions.

A series of plots was established on the 22° slope on August 18 to study grass germination under nonirrigated conditions. From the time of establishment until October 4, a total of 2.18 inches of rain fell. Maximum rainfall for any one period was 0.68 inch, and the maximum average intensity was 0.20 inch an hour. The straw-mulched plots showed germination a day or two prior to the conditioner-treated plots. Grass growth and appearance on October 4 were about the same for both type plots, and both gave a better rate of germination than control plots.

Results of field tests indicate that the effect of the conditioners was similar to that obtained on the special controlled plots. Yet to be defined are the limits of soil textures on which the chemicals will be effective and the limits of rainfall.

Inspection and comparison of grass roots from each set of plots, including both irrigated and nonirrigated, showed no significant difference in size or development. At the rate of conditioner application used, CRD-189-A has so far had no deleterious effect upon vegetation; in fact, grass appearance in most cases was superior to that on controls and mulched plots. Test plots are now being subjected to winter exposure.

Comparison of mulch and conditioner costs "in place" may best be made on the basis of the particular terrain and location under consideration. At present, it is believed that where the cost of mulch application is high, or where the cost of the mulch is excessive because of transportation, the soil conditioners will offer an advantage.

Formulation studies for obtaining improved performance which will reduce costs are now being conducted.

SUMMARY AND CONCLUSIONS

Preliminary tests indicate surface soil can be satisfactorily stabilized to the erosive action of rainfall by treating the surface with hydrolyzed polyacrylonitrile. This application serves as a temporary method for controlling erosion until vegetation can become established. The permeable film of soil conditioner, in addition to stabilizing the soil, was found to reduce runoff. Performance of the chemical was approximately the same as that of straw mulch for minimizing soil losses and reducing runoff.

Application of $\frac{1}{2}$ to 1 pound of conditioner per 100 square feet has in most cases provided satisfactory protection to the soil. Studies are being continued to determine the economics of the application and the limitations of performance due to soil composition and rainfall. Practical applications of interest are those for the temporary stabilization of slopes in almost any landscape project.

MECHANISM OF CLAY AGGREGATION BY POLYELECTROLYTES

R. A. RUEHRWEIN AND D. W. WARD¹

Central Research Laboratories, Monsanto Chemical Company

It has been pointed out in the literature (1) that the mechanism of the formation of soil aggregates is one of the most important phases of the soil-structure problem and, furthermore, that the stability of the aggregates is one of the major factors involved in forming and preserving good structural relationships in soil.

Since synthetic polyelectrolytes have a striking effect on the aggregation of soil, the mechanism of the phenomenon has been studied. This is a report of the results of the investigation in which some of the interactions of polyelectrolytes with clay have been determined. Clays were chosen for study because they are a major component of most soils of interest; they are fairly well-defined chemically and physically; and they play a prominent role in aggregate formation in soils.

The following experimental methods were employed: (a) x-ray diffraction by montmorillonite clay treated with polyelectrolytes; (b) measurement of adsorption of polymers by kaolinite clay; and (c) flocculation of clay suspensions by polymers. From the combined results of these experiments it is possible to obtain an insight into the mechanism of the stabilizing action of polyelectrolytes on clays.

MATERIALS AND METHODS

Polyelectrolytes

The polymers employed were sodium polymethacrylate, a representative polyanion, and poly β -dimethylaminoethylmethacrylate hydroacetate (DMAEM), a representative polycation. The structures of these compounds are shown in figure 1. In water solution these materials dissociate to give a highly negatively charged polymer and a highly positively charged polymer, respectively. They were prepared by conventional vinyl polymerization techniques. From light-scattering measurements, the weight average degree of polymerization of the polyanion was 15,000.

Another polycation, polyvinylbutylpyridonium bromide, was prepared by the method of Edelson and Fuoss (3).

X-ray diffraction

Montmorillonite (Wyoming bentonite) was stirred into a water solution of polyelectrolyte, the water then removed by evacuation at room temperature, and the clay finally dehydrated in a vacuum desiccator over P_2O_5 . Samples of the impregnated clay were sealed into glass capillary tubes, diffraction patterns were obtained, and the characteristic *c*-axis spacing of the montmorillonite was measured.

¹ The authors thank A. H. Herzog for the x-ray measurements and J. E. Fields for some of the polymer preparations.

Adsorption measurements

The adsorption experiments were carried out by shaking a dilute suspension of kaolinite (Cherokee clay, Georgia Coating Clay Company, used as received) in an aqueous solution of sodium polymethacrylate, centrifuging to remove the clay from the supernatant solution, and analyzing the solution for remaining polymer.

The sodium polymethacrylate was analyzed by taking advantage of the coprecipitation of the polyanion with a polycation, as described by Fuoss and Sadek (4). The scheme consisted of adding a given amount of polycation (poly β -dimethylaminoethylmethacrylate hydroacetate) to the solution of sodium polymethacrylate buffered to pH 7 with citrate-phosphate buffer. Under reproducible conditions of stirring while mixing, the precipitate formed as a dispersed fine suspension, the turbidity of which could be reproducibly measured with a sensitive light-scattering photometer. A working curve of turbidity versus polyanion concentration was established. Polymer concentrations down to about 1 ppm

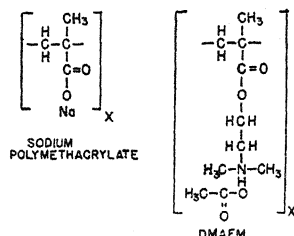


FIG. 1. STRUCTURES OF POLYELECTROLYTES

could be detected by this method, and it is believed that the adsorption data are accurate to within about 5 per cent for the most part.

Flocculation

The flocculation experiments were carried out with a 4 gm./liter kaolinite suspension in a series of 25-ml. graduated cylinders containing the flocculating reagents in increasing concentrations. The sediment volume was noted at time intervals, and the concentration increment over which a marked increase in sediment volume occurred gave the upper and lower limits of the flocculation concentration of the reagent. To eliminate errors due to contaminating electrolytes, it was necessary to use thoroughly washed clay and redistilled water in the sedimentation experiments.

RESULTS AND DISCUSSION

The cations adsorbed between the layers in a particle of montmorillonite can be replaced or exchanged with other cations including organic cations as demonstrated by Gieseking (5) and by Hendricks (6). These workers have shown that the *c*-axis spacing of montmorillonite treated with organic cations was greater than the spacing of montmorillonite containing the smaller inorganic cations.

X-ray diffraction patterns were obtained on montmorillonite treated with the polyanion sodium polymethacrylate and with the polycation DMAEM. The data on the observed *c*-axis spacing measurements are summarized in table 1 and they show that the interplanar spacing is not increased upon treatment of montmorillonite with the polyanion, whereas the spacing is increased in polycation-treated clay.

These results demonstrate that the polycation is adsorbed on the faces of the montmorillonite layers, probably by means of cation exchange. Since the faces

TABLE 1
C-axis spacing of montmorillonite treated with polyelectrolytes

POLYMER	POLYMER PER CLAY	DISTANCE
	gm.	Å.
Sodium polymethacrylate.....	0	9.7-10.1
Sodium polymethacrylate.....	0.01	9.8
Sodium polymethacrylate.....	0.54	9.9
DMAEM.....	0.035	11.8
DMAEM.....	0.075	11.4
DMAEM.....	0.202	12.8
DMAEM.....	0.665	14.4

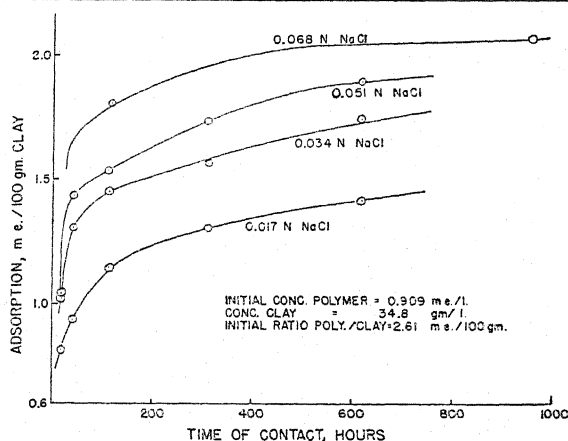


FIG. 2. ADSORPTION OF SODIUM POLYMETHACRYLATE ON KAOLINITE

of the montmorillonite layers have no sites for anion adsorption, polyanions will not adsorb thereon. It is not unlikely, however, that polyanions do adsorb by means of anion exchange on the edges of the montmorillonite layers where anion-exchange sites do occur.

In the preliminary experiments on measuring the adsorption of sodium polymethacrylate on kaolinite, it was found that the extent of adsorption depended upon time and also upon the concentration of extraneous electrolyte such as sodium chloride present in the solution. Accordingly, a series of experiments were carried out to study these two variables. The results are summarized in figure 2.

The data are expressed in milliequivalents of polymer adsorbed per 100 gm. of clay where the equivalent weight of sodium polymethacrylate is the molecular weight of a monomer unit.

The adsorption process is strikingly slow; more than a month is required for an approach to equilibrium even under the favorable conditions of these experiments. The rate-determining step in the adsorption is likely due to the rate of diffusion and orientation of the large polymer molecules. The data show, however, that the adsorption is about three quarters complete in a day, and from sedimentation experiments discussed later it is evident that an appreciable amount of adsorption occurs in only a few hours.

The increased adsorption of polymer in the presence of extraneous electrolyte may be explained on the following basis. The added sodium chloride furnishes sodium ions that form an ion cloud around the highly negatively charged polymer molecule. The ion cloud diminishes the repulsive force between two polymer molecules so that the two can be adsorbed more closely together on the clay sur-

TABLE 2
Adsorption of sodium polymethacrylate on kaolinite in presence of 0.0681 N NaCl

POLYMER CONC.	CLAY CONC.	INITIAL POLYMER/CLAY	TIME	FINAL FREE POLYMER/CLAY	ADSORPTION
<i>me./l.</i>	<i>gm./l.</i>	<i>me./100 gm.</i>	<i>hr.</i>	<i>me./100 gm.</i>	<i>me./100 gm.</i>
0.568	33.50	1.70	480	0.07	1.63
0.909	34.79	2.62	960	0.55	2.07
0.908	13.38	6.80	1270	4.78	2.02
0.909	13.27	6.86	980	4.89	1.97
0.908	6.73	13.50	360	11.64	1.86

face. This allows for a closer packing of polymer on the clay surface and hence more adsorption of the polymer.

In attempts to measure the adsorption with no electrolyte added, the extent of adsorption was found to be very low after a short contact time. After longer contact times the analysis of residual polymer in the supernatant solution was prevented by the formation of a coagulated, flocculent precipitate rather than a finely dispersed one upon addition of the polycation reagent.

Further adsorption experiments were carried out to test the dependence of the degree of adsorption upon the initial ratio of polymer to clay. These measurements were made extensively at only one concentration of added sodium chloride, 0.0681 *N*, and were run long enough to approach equilibrium adsorption. The results are summarized in table 2. They demonstrate that the clay becomes saturated with about 2.0 me. of polymer per 100 gm. More polymer is not adsorbed even in presence of a many-fold excess of polymer. Less than the saturation amount of polymer is virtually completely adsorbed.

Similar experiments with no added electrolyte but run only for a few hours also showed that polymer adsorption was complete at levels of polymer less than about 0.3 me. per 100 gm. of clay.

One of the more interesting results of the adsorption experiments is that the saturation level of polymer is close to the anion-exchange capacity of the clay, 3-15 me./100 gm. Although the anion-exchange capacity of this kaolinite has not been determined, it is presumed to be about the same as the cation-exchange capacity for kaolinite, as Marshall (7, p. 132) concludes from the work of Dean and Rubins (2). Furthermore, as the polymer saturation level would likely be increased by further addition of extraneous electrolyte, it is not unreasonable to conclude that the saturation level of the polyanion is equal to the anion-exchange capacity of the clay. This may be taken as evidence that polyanions adsorb on clay by means of anion exchange.

Since polyelectrolytes are highly charged molecules, it was thought that they would likely have a marked influence on the colloidal properties of clay. Accordingly, the flocculation of clay suspensions by polyelectrolytes was investigated.

The flocculation concentrations of several cations are shown in table 3. The water-soluble polycations are strikingly effective clay-flocculating agents as compared with the simple cations, and they obey the Schulze-Hardy rule, which

TABLE 3
Flocculation of 4 gm./l. kaolinite suspension by cations

CATION	FLOCCULATION CONCENTRATION
	<i>eq./l. $\times 10^3$</i>
Na ⁺	1300-2700
Ca ⁺⁺	430-500
Al ⁺⁺⁺	400-600
DMAEM.....	5-20
Polyvinylbutylpyridonium bromide.....	5-10

states that the flocculation concentration of an ion decreases rapidly with increasing valence (or charge) of the ion.

Polyanions do not flocculate a clay suspension; both the clay and the polyanion are negatively charged. In fact, the addition of sodium polymethacrylate to the extent of only 10 micronormal renders the clay more peptized, and a higher concentration of sodium ion, for example, is required to induce flocculation.

A different effect is obtained, however, if the order of addition of the polyanion and flocculating agent is reversed. Upon addition of sodium polymethacrylate to a clay suspension containing a flocculating amount of sodium ion, the rate of flocculation and sedimentation of the clay is markedly increased compared with that of the clay containing sodium ion alone. At a concentration of sodium ion of 5,500 micronormal, the acceleration of the flocculation is enhanced by increasing the polymer concentration up to 150 micronormal. At higher polymer concentrations the accelerating effect diminishes to the point where the polymer stabilizes the suspension.

It was also observed that the clay floccules that were sedimented upon addition of polymer were markedly resistant to redispersion. This was demonstrated further in the following experiment.

Two suspensions of 6 gm./l. of clay containing 8,200 micronormal sodium chloride (sufficient to flocculate) were prepared, and to one of them was added sodium polymethacrylate to a concentration of 13 micronormal. After standing several hours, the two suspensions were divided, one half was diluted 250-fold with water and the other half diluted 250-fold with 13 micronormal sodium polymethacrylate. The purpose of the dilution was to lower the concentration of sodium ion well below the flocculation concentration. The clay sediment was resuspended by gentle stirring, and the turbidities of the four suspensions were

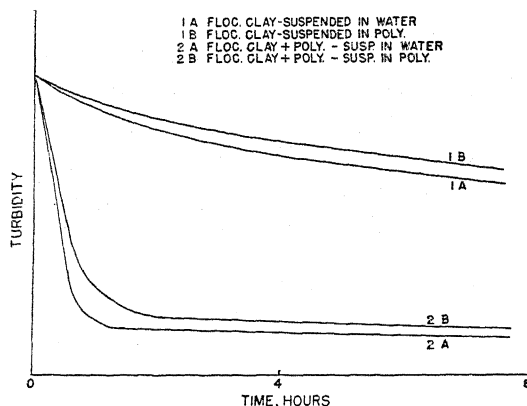


FIG. 3. STABILIZATION OF CLAY AGGREGATES

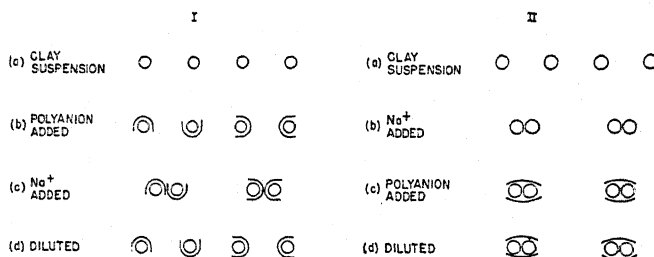


FIG. 4. SCHEMATIC REPRESENTATION OF ADSORPTION OF POLYANION ON (I) DISPERSED CLAY AND (II) FLOCCULATED CLAY

then followed for a number of hours as sedimentation was occurring. The results are shown in figure 3. A rapid decrease in the turbidity of the suspension indicates large clay particles (flocules) which sediment rapidly.

The turbidity of a dispersed clay suspension (curve 1 A) decreases slowly. The suspension that contained no polymer initially but was diluted with polymer solution (curve 1 B) is also in the dispersed state. In contrast, the two suspensions initially treated with polymer remain flocculent upon dilution (curves 2 A and 2 B).

The floc-stabilizing action of polycations has also been shown in similar experiments with DMAEM.

The clay-sedimentation experiments with polymers may be interpreted by the assumption of formation of polymer bridges between clay particles holding the particles together. Upon addition of polyanion to a dispersed dilute clay suspension, the clay particles are far apart; a polymer molecule adsorbs on only a single clay particle, and no bridges are formed. In a flocculent suspension, clay particles are sufficiently close together for adsorption of a long polymer molecule upon more than one particle, thus binding the particles together. This is represented diagrammatically in figure 4. The bound floccules are stable and are not redispersed in a medium containing no flocculating agent.

The acceleration of sedimentation of clay upon addition of polyanions may also be explained on the basis of bonding by the polymer. The formation of bridges between adjacent particles that are in the process of flocculating prevents the particles from flying apart again in their kinetically random movement, and hence the over-all rate of flocculation is increased.

It is possible for sodium polymethacrylate to bridge between two clay particles, since the molecules are several thousand Angstrom units long, comparable to the dimensions of a clay particle. Furthermore, the polymer is strongly adsorbed on clay and therefore can form strong anchor points for the bridges. ✓

For a given heat of adsorption, the adsorption of the polyanion on clay is favored over that of simple ions, because of the considerably smaller entropy of adsorption of the polyelectrolyte.

Synthetic polyelectrolytes, in addition to providing an excellent means of stabilizing aggregation in soils, offer a new method for the study of the soil-structure problem.

SUMMARY

Polycations, but not polyanions, are adsorbed in the interplanar spacing of the expanding lattice clay montmorillonite.

Sodium polymethacrylate, a polyanion, is slowly adsorbed on kaolinite clay up to a level of about 2 me. per 100 gm. The degree of adsorption depends somewhat upon the concentration of extraneous electrolyte.

Polycations are very effective flocculating agents and floc-stabilizing agents for clay. Polyanions are not flocculating agents, but they are effective stabilizing agents for flocculated clay.

Sodium polymethacrylate functions as a stabilizing agent of clay aggregates by binding the particles together. The polymer molecules are sufficiently long to bridge the gap between clay particles, and they are capable of strongly adsorbing on the clay to form anchor points for the bridge. The adsorption process is probably one of ion exchange.

REFERENCES

- (1) BAVER, L. D. 1948 Soil Physics. John Wiley and Sons, New York
- (2) DEAN, L. A., AND RUBINS, E. J. 1947 Anion exchange in soils: I. *Soil Sci.* 63: 377-386.
- (3) EDELSON, D., AND FUOSS, R. M. 1950 A contrast between polyelectrolytes and simple electrolytes. *Jour. Amer. Chem. Soc.* 72: 306-310.

- (4) FUOSS, R. M., AND SADEK, H. 1949 Mutual interaction of polyelectrolytes. *Science* 110: 552-554.
- (5) GIESEKING, J. E. 1939 Mechanism of cation exchange in the montmorillonite-beidelite-nonttronite type of clay minerals. *Soil Sci.* 47: 1-13.
- (6) HENDRICKS, S. B. 1941 Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals forces. *Jour. Phys. Chem.* 45: 65-81.
- (7) MARSHALL, C. E. 1949 The Colloid Chemistry of the Silicate Minerals. Academic Press Inc., New York.

AUTHOR INDEX

- Aldrich, D. G., and Martin, J. P. Chemical changes with soil fumigation, 149-159.
- Allison, L. E. Structure of saline and alkali soils, 443-454.
- Axley, J. H. *See* Hoyert, J. H.
- Baker, G. O. *See* Jordan, J.
- Barber, S. A., and Marshall, C. E. Ionization of soils and soil colloids, 403-413.
- Bartholomew, W. V., and Hiltbold, A. E. Recovery of fertilizer nitrogen by oats, 193-201.
- Bavel, C. H. M. van. Gaseous diffusion in porous media, 91-104.
- Beacher, R. L., Longenecker, D., and Merkle, F. G. Form, fineness, and amount of limestone, 75-82.
- Bear, F. E. *See* Ririe, D.
- Black, C. A. *See* Jackman, R. H.
- Blume, J. M. Effect of radiophosphorus on plants, 299-303; leaching studies with radiocalcium, 383-389.
- Bower, C. A., Reitemeier, R. F., and Fireman, M. Analysis of saline and alkali soils, 251-261.
- Bradfield, R. *See* Schmehl, W. R.
- Bramao, L., Cady, J. G., Hendricks, S. B., and Swerdlow, M. Minerals in clays and soils, 273-287.
- Burnett, E. *See* Martin, W. P.
- Cady, J. G. *See* Bramao, L.
- Campbell, R. B. Freezing point of water, 221-229.
- Cernuda, C. F. *See* Smith, R. M.
- Colter, W. G. *See* Weeks, L. E.
- Comar, C. L. *See* Harris, H. C.
- Corey, G. *See* Jordan, J.
- Corley, T. E. *See* Jamison, V. C.
- Dalton, J. D., Russell, G. C., and Sieling, D. H. Organic matter and phosphate, 173-181.
- Dean, L. A. *See* Fried, M.; Shaw, E.
- Dole, M. W. Determining copper in soils, 135-147.
- Engibous, J. C. *See* Martin, W. P.
- Erdman, L. W., and Means, U. M. Yield and nitrogen content of legumes, 231-235.
- Fireman, M. *See* Bower, C. A.
- Fried, M., and Dean, L. A. Measuring available soil nutrients, 263-271.
- Gardner, W., and Kirkham, D. Neutron method for soil moisture, 391-401.
- Gross, H. M. *See* Thomas, R. P.
- Harris, H. C., MacIntire, W. H., Comar, C. L., Shaw, W. M., Winterberg, S. H., and Hood, S. L. Calcium migrations in soils and plants, 289-298.
- Hassan, M. N., and Overstreet, R. Seedling test of alkali soils, 315-326.
- Hedrick, R. M., and Mowry, D. T. Polyelectrolytes and soil structure, 427-441.
- Hendricks, S. B. *See* Bramao, L.
- Hiltbold, A. E. *See* Bartholomew, W. V.
- Hood, S. L. *See* Harris, H. C.
- Hoyert, J. H., and Axley, J. H. Liming materials and pH of Maryland soils, 61-69.
- Jackman, R. H., and Black, C. A. Phytase activity in soils, 117-125; hydrolysis of phytate phosphorus, 167-171.
- Jamison, V. C., Reed, I. F., Stokes, C. M., and Corley, T. E. Effect of tillage depth, 203-210.
- Jones, L. W. Effect of DDT on soil microorganisms, 237-241.
- Jordan, J., Simkins, C., Corey, G., Knight, R., and Baker, G. O. Movement of fertilizer phosphorus, 305-313.
- Kirkham, D. *See* Gardner, W.
- Klute, A. Solving flow equation for water, 105-116.
- Knight, R. *See* Jordan, J.
- Krone, R. B., Ludwig, H. F., and Thomas, J. Device for sampling soil solutions, 211-219.
- Longenecker, D. *See* Beacher, R. L.
- Longenecker, D., and Merkle, F. G. Placement of lime compounds, 71-74.
- Ludwig, H. F. *See* Krone, R. B.
- McCreery, R. A. *See* Smith, H. W.
- MacIntire, W. H. *See* Harris, H. C.
- Marshall, C. E. *See* Barber, S. A.
- Martin, J. P. *See* Aldrich, D. G.
- Martin, W. P., Taylor, G. S., Engibous, J. C., and Burnett, E. Soil and crop response in the field, 455-471.
- Means, U. M. *See* Erdman, L. W.
- Mehlich, A. Effect of colloids on calcium release, 361-374.
- Merkle, F. G. *See* Beacher, R. L.; Longenecker, D.
- Meyer, T. A., and Volk, G. W. Effect of particle size of limestones, 37-52.
- Mitra, R. P., and Rajagopalan, K. S. Base-exchange capacity of clays, 349-360.
- Moodie, C. D. *See* Smith, H. W.

- Mowry, D. T. *See* Hedrick, R. M.
Newton, H. P., and Toth, S. J. Response of crop plants to I and Br., 127-133.
Overstreet, R. *See* Hassan, M. N.
Peech, M., *See* Schmehl, W. R.
Quastel, J. H. Soil aeration and structure, 419-426.
Rajagopalan, K. S. *See* Mitra, R. P.
Reed, I. F. *See* Jamison, V. C.
Reitemeier, R. F. *See* Bower, C. A.
Reuther, W., Smith, P. F., and Specht, A. W. Cation accumulation in citrus soils, 375-381.
Ririe, D., and Toth, S. J. Plant studies with radioactive calcium, 1-10.
Ririe, D., Toth, S. J., and Bear, F. E. Movement of lime and gypsum in soil, 23-35.
Ruehrwein, R. A., and Ward, D. W. Mechanism of aggregation, 485-492.
Russell, G. C. *See* Dalton, J. D.
Schmehl, W. R., Peech, M., and Bradfield, R. Calcium absorption from acid soils, 11-21.
Shaw, E., and Dean, L. A. Estimating available zinc in soils, 341-347.
Shaw, W. M. *See* Harris, H. C.
Sieling, D. H. *See* Dalton, J. D.
Simkins, C. *See* Jordan, J.
Smith, H. W., McCreery, R. A., and Moodie, C. D. Collecting and preserving profiles, 243-248.
Smith, P. F. *See* Reuther, W.
Smith, R. M., and Cernuda, C. F. Macrostructure of Puerto Rican soils, 183-192.
Specht, A. W. *See* Reuther, W.
Stokes, C. M. *See* Jamison, V. C.
Swerdlow, M. *See* Bramao, L.
Taylor, G. S. *See* Martin, W. P.
Taylor, S. A. Soil moisture tension in root zone, 331-339.
Thomas, J. *See* Krone, R. B.
Thomas, R. P., and Gross, H. M. Reacting rates of limestone particles, 53-59.
Toth, S. J. *See* Newton, H. P.; Ririe, D.
Volk, G. W. *See* Meyer, T. A.
Vries, D. A. de. Measuring thermal conductivity in situ, 83-89.
Ward, D. W. *See* Ruehrwein, R. A.
Weeks, L. E., and Colter, W. G. Control of erosion, 473-484.
Winterberg, S. H. *See* Harris, H. C.

SUBJECT INDEX

- Acidity, influence on calcium absorption by alfalfa, 11-22.
- Aeration—
 algenic acid, 422.
 as affected by—
 organic matter, 419-426.
 polyelectrolytes, 427-441.
 factors, 423.
- Aggregate—
 effect of polyuronides and polysaccharides, 421.
 mechanism of formation, 485-492.
 size relations, 189.
 stability, 186, 430.
- Aluminum, effect on calcium absorption, 18.
- Ammonia, as affected by—
 DDT, 238.
 fumigation, 151.
- Aspergillus niger* method—
 comparison with chemical methods, 142.
 for determining copper in soils, 135-148.
 influence of physical factors, 138.
 mycelial weight and calcium contents, 139.
- Autoradiographs—
 alfalfa, Ca45, 6.
 oats, Ca45, 5.
 red clover, Ca45, 7.
 tomatoes, Ca45, 8.
- Availability of calcium salts, 2.
- Available nutrients, measurement in soils, 263-271.
- Base-exchange capacity—
 of—
 illite, 355.
 kaolinite, 355.
 mica, 355.
 origin in clays, 349-360.
- Books, *see* end of letter B.
- Bromine—
 contents of tomatoes, 132.
 response of crop plants to, 127-134.
- BOOKS**
- Advances in Agronomy, 161.
 African Soils, 415.
 Agronomy, Advances in, 161.
 Agronomy, Handbook of Ohio Experiments in, 327.
 Ahlgren, G. H., Klingman, G. C., and Wolf, D. E. Principles of Weed Control, 165.
 Allen, O. N. Experiments in Soil Bacteriology, rev. ed., 162.
 American Economy, 327.
 Animal Agriculture, Proceedings First National Institute of, 329.
 Animal Nutrition, 161.
 Annual Review of Microbiology, 161.
 Association of American Control Officials, Official Publication No. 5, 328.
 Bacteria, symbiotic, Contribution à l'Étude de la Symbiose Bactérienne chez les Légumineuses, 415.
 Bacterial Physiology, 249.
 Bainer, R. *See* Barger, E. L.
 Barger, E. L., Carleton, W. M., McKibben, E. G., and Bainer, R. Tractors and Their Power Units, 418.
 Barker, H. A. *See* Clifton, C. E.
 Bibliography of Differential Thermal Analysis, 327.
 Biology, Man and the Living World, 328.
 Bonner, J., and Galston, A. W. Principles of Plant Physiology, 417.
 British Scientists, 162.
 Brown, A. F. Y. American Economy, 327.
 Carleton, W. M. *See* Barger, E. L.
 Carlson, F. A. Geography of Latin America, ed. 3, 416.
 Chemistry and Technology of Food and Its Products, 249.
 Chiang, Y. *See* Smothers, W. J.
 Christensen, C. M. Molds and Man, 164.
 Clifton, C. E., Raffel, S., and Barker, H. A. (Editors) Annual Review of Microbiology, vol. 5, 161.
 Consolidation and Settlement of Loaded Soil Layers, 164.
 Contribution à l'Étude de la Symbiose Bactérienne chez les Légumineuses, 415.
 Demolon, A. Contribution à l'Étude de la Symbiose Bactérienne chez les Légumineuses, 415.
 Desert Year, 415.
 Design and Analysis of Experiments, 415.
 Differential Thermal Analysis, Bibliography of, 327.
 Elements of Plant Protection, 162.
 Elliott, C. Manual of Bacterial Plant Pathogens, ed. 2, 163.
 Enzymes, Chemistry and Mechanism of Action, 416.
 Essays in Provocation, 327.
 Experiments in Soil Bacteriology, 162.
 Fassett, N. C. Grasses of Wisconsin, 162.
 Fenton, F. A. Field Crop Insects, 416.
 Fertilizer Application, Proceedings of the Twenty-Seventh Annual Meeting of the National Joint Committee on, 417.
 Field Crop Insects, 416.
 Field Crops, 249.
 Food and Its Products, Chemistry and Technology of, 249.
 Fungi, Molds and Man, 164.
 Galston, A. W. *See* Bonner, J.
 Gardening in Florida, Subtropical, 330.
 Geography of Latin America, 416.
 Grasses of Wisconsin, 162.
 Greene, L. S., and Williamson, R. deV. (Editors) Resources and Policy. Current Issues in Conservation, 165.
 Handbook of Ohio Experiments in Agronomy, 327.
 Harrison, C. M. *See* Rather, H. C.
 Hellenelund, K. V. Consolidation and Settlement of Loaded Soil Layers, 164.
 Holmyard, E. J. British Scientists, 162.
 Hoover, G. E. Essays in Provocation, 327.
 Hyams, E. Soil and Civilization, 417.
 Illingworth, F. North of the Circle, 328.
 International Index of Films on the Conservation and Utilization of Resources, 163.

BOOKS (*continued*)

- Jacobs, M. M. (Editor) *Chemistry and Technology of Food and Its Products*, vol. 3, rev., 249.
- Japan, Northern Honshu Area, Reconnaissance Soil Survey of, 329.
- Kemphorne, O. *Design and Analysis of Experiments*, 415.
- Klingman, G. C. *See* Ahlgren, G. H.
- Krutch, J. W. *Desert Year*, 415.
- Latin America, *Geography of*, 416.
- McKibben, E. G. *See* Barger, E. L.
- Man and the Living World, 328.
- Manual of Bacterial Plant Pathogens, 163.
- Manual of Phycology, 163.
- Maynard, L. A. *Animal Nutrition*, ed. 3, 161.
- Microbial Decomposition of Cellulose, 164.
- Microbiology, *Annual Review of*, 161.
- Mineral Nutrition of Plants, 250.
- Molds and Man, 164.
- Mortlock, H. C. *Reconnaissance Soil Survey of Japan, Northern Honshu Area*, 329.
- Myrbäck, K. *See* Sumner, J. B.
- Norman, A. G. (Editor) *Advances in Agronomy*, vol. 3, 161.
- North of the Circle, 328.
- Official Publication, Association of American Control Officials, No. 5, 328.
- Phosphates in Agriculture, 329.
- Phycology, *Manual of*, 163.
- Plant Growth Substances, 164.
- Plant Pathogens, *Manual of Bacterial*, 163.
- Plant Physiology, *Principles of*, 417.
- Plant Protection, *Elements of*, 162.
- Plants, *Mineral Nutrition of*, 250.
- Principles of Plant Physiology, 417.
- Principles of Weed Control, 165.
- Proceedings, First National Institute of Animal Agriculture, 329.
- Proceedings of the Twenty-Seventh Annual Meeting of the National Joint Committee on Fertilizer Application, 417.
- Pyenson, L. *Elements of Plant Protection*, 162.
- Raffel, S. *See* Clifton, C. E.
- Range Management, *Principles, and Practices*, 329.
- Rather, H. C., and Harrison, C. M. *Field Crops*, ed. 2, 249.
- Reconnaissance Soil Survey of Japan, Northern Honshu Area, 329.
- Resources and Policy. *Current Issues in Conservation*, 165.
- Sampson, A. W. *Range Management, Principles, and Practices*, 329.
- Sauchelli, V. *Phosphates in Agriculture*, rev. ed., 329.
- Sin, R. G. H. *Microbial Decomposition of Cellulose*, 164.
- Skog, F. (Editor). *Plant Growth Substances*, 164.
- Smiley, N. *Subtropical Gardening in Florida*, 330.
- Smith, G. M. (Editor) *Manual of Phycology*, 163.
- Smothers, W. M., Chiang, Y., and Wilson, A. *Bibliography of Differential Thermal Analysis*, 327.
- Soil and Civilization, 417.
- Soil Bacteriology, *Experiments in*, 162.
- Soil Survey of Japan, Northern Honshu Area, Reconnaissance, 329.
- Soil Testing in the United States, 418.
- Soils, African, 415.
- Stanford, E. E. *Man and the Living World*, ed. 2, 328.
- Subtropical Gardening in Florida, 330.
- Sumner, J. B., and Myrbäck, K. (Editors) *Enzymes, Chemistry and Mechanism of Action*, vol. 2, part 2, 416.
- Tohoku Journal of Agricultural Research, vol. 1, no. 2, 330.
- Tractors and Their Power Units, 418.
- Truog, E. (Editor) *Mineral Nutrition of Plants*, 250.
- Weed Control, *Principles of*, 165.
- Werkman, C. H., and Wilson, P. W. (Editors) *Bacterial Physiology*, 249.
- Williamson, R. de V. *See* Greene, L. S.
- Wilson, A. *See* Smothers, W. J.
- Wilson, P. W. *See* Werkman, C. H.
- Wolf, D. E. *See* Ahlgren, G. H.
- Calcium—
 content of—
 alfalfa, 12.
 crimson clover, 295.
 oats, 295.
 red clover, 295.
 rye grass, 294.
 effect of iron and aluminum oxides on release, 361-374.
 ion activities, 406.
 leaching from sandy loam, 383-389.
 losses from soils by leaching, 25, 386.
 migrations in soils and plants, 289-298.
 movement in tomatoes, 6.
 plant studies with Ca⁴⁵, 1-10.
- Calcium-magnesium ratios—
 effect of calcitic and dolomitic limestones on—
 alfalfa, 45.
 soybean hay, 46.
 in soils as related to that in plants, 49.
- Carbon dioxide production, relation to phytase activity, 121.
- Cation-anion exchange—
 effect of iron and aluminum oxides, 361-374.
 properties of soils, 366.
- Cation-exchange capacity—
 determination with sodium, 258.
 origin of, in clays, 349-360.
 relation to pH, 259.
- Chlorine—
 content of—
 buckwheat, 130.
 soils, as affected by fumigation, 153.
 tomatoes, 129.
 distribution in tomato plant fractions, 130.
- Citrus soils, accumulation of bases and heavy metals in relation to phosphorus fertilization, 375-381.

- Clays—
cation-exchange capacities, 355.
characterization of kaolinite, halloysite, and related minerals, 273-288.
origin of base-exchange capacity, 349-360.
titration curves, 351.
- Conductivity of sand at various moisture contents, 110.
- Copper, *Aspergillus niger* method for estimating, in soils, 135-148.
- DDT—
recovery of from soils, 239.
stability, 237-242.
- Differential thermal analyses—
halloysites, 277.
kaolinites, 275.
soil clays, 277.
- Diffusion—
alcohol vapor, 102.
tube, 95.
- Electron micrographs—
halloysite, 279.
kaolinites, 279.
soil clays, 280-281.
- Erosion control, use of polyelectrolytes, 473-484.
- Exchangeable cations—
analyses of saline and alkali soils, 251-262.
effect of fumigation, 152.
influence of liming materials, 41.
- Fertilizer placement methods, comparison, 266.
- Flow equations for water, method for solving, 105-116.
- Freezing point—
alternate freezing and thawing, 224.
water in puddled and unpuddled soils, 221-230.
- Fumigation, effect on chemical properties of soils, 149-159.
- Gaseous diffusion—
experimental assembly, 96.
in porous media, 91-104.
- Gypsum—
effect on exchange potassium and sodium, 31.
movement and effect on soil, 23-36.
- Hydrogen—
effect of particle size of limestone, 42.
effect on calcium absorption, 18.
- Iodine—
contents of—
buckwheat, 130.
tomatoes, 129.
- distribution in fractions of tomato plants, 130.
response of crop plants to, 127-134.
- Ionization of soils and soil colloids, potassium-calcium relationships in illite, kaolinite, and halloysite, 403-413.
- Lime—
influence of form, fineness, and amount on plant development, 75-82.
losses of incorporated calcium, 292.
movement in soil, 23-36.
placement, effects on root growth, 71-74.
requirements of soils, 66.
residual effects, 76.
- Liming materials—
effect on—
exchange potassium and sodium, 31.
exchangeable cations, 41.
pH values of soils, 61-70.
movement within soils, 28.
- Magnesium losses from soil by leaching, 25.
- Manganese—
as affected by fumigation, 154.
effect of calcium absorption, 18.
- Methods—
copper in soil, 135-148.
exchangeable cations in saline and alkali soils, 251-262.
reacting rates of different particle sized limestones, 53-60.
sampling soil solutions, 211-220.
soil moisture by neutron scattering, 391-401.
solving flow equation for water, 105-116.
thermal conductivity of soil, 83-90.
zinc status of soils, 341-347.
- Microbial activities, as affected by DDT, 237-242.
- Moisture tensions—
at various depths, 332.
changes in, 332.
curves, 222.
estimating in root zone of growing crops, 331-339.
freezing point of water at various, 221-230.
relation to phosphorus content of potatoes, 308.
- Neutron, soil moisture estimation, 391-401.
- Nitrates—
as affected by DDT, 239.
soil, effect of fumigation, 151.
- Nitrogen—
content of—
legumes, 233.

- Nitrogen, content of—*continued*.
 oats, 195.
 in soil extracts, 198.
 recovery of fertilizer, by oats, 193-201.
 use of total yields for predicting, 231-236.
- Organic matter—
 effect on phosphorus availability, 173-181.
 influence on aeration and structure, 419-426.
- Particle size of limestones, effect on reaction, cations, and growth, 37-52.
- pH—
 as affected by—
 liming materials, 61-70.
 phytase activity, 121.
 influence of particle size, 39.
- Phosphorus—
 accumulation of bases and heavy metals in citrus soils treated with, 375-381.
 derived from fertilizer and soil by plants, 301, 309.
 effect of organic matter on, in soils, 173-181.
 HCl-soluble in soils, 168.
 hydrolysis of phytase, 167-171.
 uptake and movement of fertilizer, 305-314.
 uptake by plants, 175.
- Phytase—
 activity in soils, 117-126.
 as affected by—
 microbial activity, 119.
 moisture content, 122-123.
 pH values, 121.
 hydrolysis of, phosphorus in soils, 167-171.
 measuring, 117.
- Polyelectrolytes, effect on—
 clay aggregation, 485-492.
 soil properties, 427-441.
 structure of saline and alkali soils, 443-454.
- Porosity—
 alcohol, 102.
 effect of depth of tillage, 206.
 in porous media, 91-104.
- Potassium—
 ion activities, 406.
 losses from soil by leaching, 25.
- Pulvini, absence of calcium, 7.
- Radiation effects on plants grown with P32, 299-304.
- Radioisotopes—
 Ca45, 1-10, 11-22, 23-36, 289-298, 383-389.
 P32, 299-304, 305-314.
- Root development—
 cotton, effect of tillage, 208.
 influence of lime placement, 71-74.
- Saline soils, effect of polyelectrolytes, 443-454.
- Seedling test—
 effect of sodium salts, 321.
 of alkali soils, 315-326.
- Sodium—
 losses from soil by leaching, 25.
 use for determining cation-exchange capacity, 256.
- Soil conditioners—
 effect on—
 aggregation, 432.
 carrot yields, 467.
 corn yields, 463.
 erosion control, 473-484.
 moisture relationships, 432.
 potato yields, 466.
 sugar beets, 468.
 workability, 432.
 field and crop responses from, 455-471.
 synthetic, 425.
- Soil moisture, determination by neutron scattering, 391-401.
- Soil profiles, collection and preservation, 243-248.
- Soil series, analyses, descriptions of, or experiments with—
 Aguirre, 186; Amelia, 186; Appling, 285; Bayamon, 186; Beja, 275; Brookston, 456; Canfield, 38; Caribou, 265; Carrington, 186; Catalina, 186; Cecil, 285, 344, 361; Chester, 61, 301; Chilcott, 446; Chino, 222, 446; Cialitos, 186; Claibourne, 289; Clarion, 119, 168, 193, 397; Coamo, 186; Colby, 344; Collington, 57, 129; Columbia, 141; Copake, 129; Coto, 186; Crosby, 38, 456; Davidson, 265, 344; Dayton, 475; Decatur, 203, 285; Delco, 305; Dewey, 285; Duffield, 61; Edina, 168; Emory, 61; Ephrata, 346; Evesboro, 301; Fannin, 361; Felida, 141; Fort Collins, 222; Frankstown, 344; Fullerton, 285; Georgeville, 361; Glenelg, 344; Greenville, 203, 285; Hanford, 149; Hartsells, 289; Hoosic, 129; Houston, 344; Imperial, 446; Lakeland, 345; Lakewood, 129; Las Flores, 446; Lawrenceville, 129; Mardin, 11; Marion, 121; Marshall, 193; Matanzas, 186; Matawan, 61; Mattapex, 61; Mecklenburg, 285; Miami, 428, 456, 475; Monona,

- 397; Mucara, 186; Myersville, 344; Nipe, 186, 361; Norfolk, 285, 344, 383; Norton, 23, 129; O'Neil, 397; Orangeburg, 285; Pachappa, 222, 444; Palouse, 344; Paulding, 456, 475; Plummer, 141; Ponceña, 186; Putnam, 397; Ramona, 149; Red Bay, 285; Rubicon, 141; Ruston, 285; Sagemoor, 346; Santa Isabel, 186; Sassafras, 1, 23, 61, 129; Sauvie, 141; Sebrie, 444; Shelby, 344; Squires, 129; Timmermon, 346; Utuado, 186; Wabash, 397; Washington, 129; Westmoreland, 75; White Store, 361; Yolo, 149.
- Soil solution, porous tube for sampling, 211-220.
- Specific moisture capacity of sand at various moisture contents, 110.
- Structure—
characterization of soil, 184.
effect of organic matter, 419-426.
of Puerto Rican soils, 183-192.
typical conditions of, 187.
- Thermal conductivity of soils—
nonstationary method, *in situ*, 83-90.
values, 88.
- Tillage depth, effect on soil conditions and cotton growth, 203-210.
- Tropical soils, macrostructure in Puerto Rico, 183-192.
- Zinc status of soils—
effect of—
grinding, 345.
heating, 346.
time of extraction, 344.
dithizone for estimating, 341-347.